IRRADIATION OF ORGANIC SYSTEMS WITH GAMMA RAYS

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CONTENTS

INTRODUCTION

Radiochemistry may be considered as dealing with the changes in atomic nuclei brought about by radiations and particles of very high energy; its origins go back to the year following the discovery of Becquerel, in 1896, that radiations from pitchblende could fog a photographic plate. Shortly after this, the radioactive elements radium and polonium were discovered by Marie and Pierre Curie, and by 1933 it was evident that radioactive forms of all the elements could be produced in the process of a nuclear transmutation. E. Fermi's work on the bombardment of uranium-239 with neutrons contributed to the discovery, in 1938, of uranium fission. During the war years the importance of the radioactive element plutonium-239, as a nuclear explosive, resulted in the construction of atomic piles to produce this element by neutron capture by uranium-239.

In recent years the longer lived radioactive products have been made available for chemical, biological and industrial research, as sources of ionising radiations. For example, caesium-137, which emits alpha-rays, has found important applications in radiotherapy; the electron-emitting isotope strontium-90 is employed in thickness gauges and static eliminators in textile work. Cobalt-60, the radiation source used in the work to be described in this thesis, emits gamma-radiation and is one of the more frequently used radio-isotopes in the study of the effects of ionising radiation on chemical systems.

Radiation chemistry is concerned with the changes induced in chemical systems by radiation from the radioactive elements, or from other short-wave radiation sources such as the van der Graaff generator. The most commonly used radiations are the very short electromagnetic radiations, X and gamma-rays, and the corpuscular

radiations made up of electrons (beta-rays), helium nuclei (alpha-rays), protons and neutrons.

The work here described is concerned with the emission of gamma-rays from cobalt-60; this type will be considered in more detail. Cobalt-60 emits gamma-rays of energy 1.12 and 1.33 MeV, and beta-rays of energy 0.31 MeV.[1] However the power of penetration of the beta-rays is very small, and their possible effects have been ignored in this work.

Gamma-rays are radiations of the same character as ultra violet or visible light, but of much shorter wavelength, and where, in photochemistry the primary process is absorption of a photon by an individual molecule, the energy of gamma-rays on the other hand is almost entirely absorbed in the ejection of electrons from the atoms through which they pass. The latter process, unlike the photochemical process, is normally independent of the manner in which these atoms are combined into molecules.

The interaction of gamma-radiation with matter results in the absorption of energy by three processes:[2-4] the photoelectric effect, the Compton effect and the pair formation effect.

At energies below 0.2 MeV the most important process is the photoelectric effect. In this process the electromagnetic quantum of energy is utilised to eject a bound electron from an atom or molecule with a kinetic energy which is the energy difference between the original quantum and the binding energy of the electron. This effect is more important for elements of high atomic number; for example, the photo-electric contribution to the total gamma-ray absorption is greater in the alkyl iodides than it is in the alkyl chlorides.

Instead of giving up its entire energy, a photon may transfer only part of its energy to an electron and the photon is degraded in energy and deflected from its original path. The process may then be repeated. This process is called the Compton effect, and it is the predominant absorption process for electromagnetic radiation.

The pair production effect, involving the formation of a positron-electron pair by a photon of at least 1.02 MeV, can be discounted, for it only assumes importance for energies very much greater than 1.33 MeV.

In passing through matter, the ejected electron may excite or ionise many of the molecules in its path:

$$M \longrightarrow M^{*} \qquad \text{or} \qquad M \longrightarrow M^{+} + e^{-}$$

After the formation of the primary ions and excited molecules, a variety of secondary processes may occur. Negative ions may be formed, and disruptions of excited molecules to radicals or new molecules may occur. Most of the chemical effects observed, result from the formation of free radicals, which may combine with each other, or react with other species of the medium, their fate being determined by the rates of the possible competing reactions.

Organic solutions have been irradiated both pure and as mixtures. The commonest types of mixture to be investigated are those with oxygen, with water, or with both. In many cases the presence of oxygen leads to results essentially different from those obtained with the pure substance, an effect which Collinson and Swallow[5] associate with the high electron affinity of oxygen. The study of dilute solutions of one substance in another introduces the concept of "indirect action".

This arises from the non-specificity of absorption of the energy of ionising radiations, from which it follows, that in a dilute solution, chemical effects on the solute are more likely to result from attack by the primary products from the solvent, rather than from a direct effect of the radiation on the solute.

Yields of products from the irradiation of chemical solutions are given in terms of G-values. These refer to the number of molecules produced, or decomposed, for each 100 electron volts of energy absorbed from the radiation source. The significant definition is usually indicated by a subscript; for example, $G_{(CCl_4)}$ refers to the formation of carbon tetrachloride, while $G_{(-CCl_4)}$ refers to the removal of the compound. G-values ranging from 0.1 to 100,000 have been recorded.

The Irradiation of Aqueous Solutions.

Aqueous solutions have been a frequent subject for study in radiation chemistry. The reactions are less complex and the mechanisms better understood than in other fields of radiation chemistry.

Water produces mainly H, OH and HO_2 radicals,[6] and the products from the irradiation of dilute aqueous organic solutions, arise from attack of these radicals on the organic molecule; for example, phenol is formed from the irradiation of a dilute aqueous benzene solution.[7]

The first systematic experiments in this field were carried out by Kailan[8], who irradiated many aqueous solutions of aliphatic and aromatic compounds. One of his first observations was that hydroxylation is the predominant reaction when aqueous aromatic solutions are exposed to the mixed beta and gamma-rays from radium. He observed the formation of ortho and paranitrophenols[9] when aqueous nitrobenzene solutions were

irradiated. Later work with X-rays[10] has shown that all three hydroxylated isomers are formed, and the same is true of chlorobenzene[11] and benzoic acid[12]. The manner in which these hydroxyl groups are introduced into the aromatic ring, independent of the group already present, suggests free radical attack rather than the usual ionic attack on the benzene nucleus.

Dehalogenation by irradiation in aqueous solution has also been observed in the following compounds: chlorobenzene, bromobenzene, ortho and para-dichlorobenzene[13], and ortho and para-dichlorophenol[14]. It is claimed that hexachlorobenzene[15] is not so dehalogenated and it has been suggested[16] that the effective process might necessitate the presence of a hydrogen atom attached to another carbon atom in the molecule.

Different types of reactions occur when aliphatic unsaturated hydrocarbons are irradiated in aqueous solution. Clay et al.[17] have shown that the irradiation of a saturated aqueous solution of ethylene with gamma-rays produces hydrogen peroxide, acetaldehyde, formaldehyde and glyoxal. In the absence of oxygen, acetaldehyde, butyraldehyde and polymer were obtained. Acetaldehyde is also obtained from the action of X-rays on aqueous ethanol solutions.[18]

According to Keller and Weiss[19], aqueous solutions of sterols show surprisingly specific reactions. Cholesterol undergoes hydroxylation of the double bond at the 5, 6-position, with some attack also occurring at the 7-position, and pregnenolone reacts similarly. Coleby et al.[20] have shown that reduced products appear when sterols are irradiated in oxygen-free aqueous solutions, but oxidised products are obtained from air saturated aqueous solutions. Stacey has suggested[21] that extended

research might reveal reactions useful in the synthesis of pharmaceuticals, where the high price of the product might offset the unfavourable G-values.

Very recently Swallow[22] has reported that a methylene blue - ethanol - acid solution, when irradiated with gamma-rays, is reduced to the same stable semi-quinone free radical as is produced by titanous chloride, and he suggests that oxidation or reduction induced by radiation could be applied in chemical analysis as a substitute for titration in certain cases.

The Irradiation of Pure Organic Compounds

The action of X-rays and alpha-particles on the hydrocarbons was studied by early workers.[23, 24] The alkanes, such as butane, pentane and hexane give rise to hydrogen gas ($G \sim 5$), and hydrocarbon products ($G \sim 1$) resulting from a splitting of the C-C bond. McCauley and Schuler[25] have shown recently, that in the radiolysis of liquid butane, in the presence of radioactive iodine acting as a radical scavenger, the distribution of alkyl iodide products indicates that a free radical and an ionic mechanism must be operating. Black[26] has observed that pile irradiation of some paraffinic hydrocarbons induces double bond formation, and Charlesby[27] has irradiated long chain paraffins ($C > 10$) in a nuclear reactor and has obtained waxes which remain solid up to 150°C. Interesting results are reported by Caffrey and Allen[28], who noted that the product distributions from the radiolysis of n-pentane adsorbed on different mineral solids, differed widely for the different solids. They postulate that a specific transfer of energy from the solid to the adsorbed pentane occurs on irradiation.

Polymer formation is the predominant process in the irradiation of the alkenes; for example, acetylene in the gas phase is polymerised by alpha particles with a G-value of 75[29], and ethylene under pressure is

polymerised with G ~ 2000 [30]. In an interesting study on a series of cis and trans-octa decenes with the double bond in various positions, Charlesby[31] has found that crosslink formation is decreased as the double bond is moved away from the end of the molecule, and that the trans stereoisomer gave higher yields of crosslinking than the cis stereoisomer.

Aromatic compounds are much more stable than aliphatic compounds to irradiation. Small yields of gases and a little polymer formation have been observed. It has been suggested[32], that absorption of energy by the aromatic molecule results in the formation of excited states, which can be resonance stabilised by the shielded system of π-electrons in the aromatic nucleus. The fluorescence of organic compounds such as anthracene, naphthalene, stilbene and terphenyl, when exposed to ionising radiations, is explained by assuming that the excited states have large probabilities for de-activation by the emission of fluorescent radiation.

Even in mixtures this "protective" influence of the benzene ring has been demonstrated; for example, the decomposition of irradiated cyclohexane-benzene solutions is much less than that of pure cyclohexane.[24,32] Burton and Lipsky[33] suggest that the benzene may be exercising a radical scavenging effect, and it may also be providing an alternative path of energy dissipation for excitation energy transfer from the cyclohexane. In support of this idea is Burton and Patrick's[34] observation that this protective effect was not observed for mixtures of propionaldehyde and hexadeuterobenzene, where there is evidence to suggest that the transfer of excitation energy from the propionaldehyde is prohibited because the lowest excited state of the propionaldehyde is believed to be beneath that of benzene. Schuler[35] has shown recently that low concentrations of solutes which have high electron affinities, such as iodine, the alkyl halides, and sulphur

dioxide, decrease the hydrogen yield in the gamma-irradiation of cyclohexane by about 40%.

An examination of the decomposition products from alpha particle bombardment of ten normal, iso and tertiary aliphatic alcohols was undertaken by McDonell and Newton[36]. Hydrogen gas, aliphatic hydrocarbons, water and carbon monoxide were formed in all cases, while the principal oxidised products were aldehydes, ketones and glycols. The products formed indicate that bond rupture occurs at the carbinol carbon atom. An elegant technique by Burr[37], who irradiated several ethanols, deuterated in different positions, and measured the deuterium content in the hydrogen production, has enabled him to conclude that the primary hydrogen atom production originates almost exclusively from the $-CH_2-$ group (process 1) and the ensuing abstraction reaction occurs principally on the -OH hydrogen (80-90%) by process 2, with a small amount occurring at the CH_3- group by process 3.

$$CH_3CH_2OH \longrightarrow CH_3\dot{C}H\,OH + H^{\bullet} \text{ ----------(1)}$$

$$CH_3CH_2OH + H^{\bullet} \longrightarrow CH_3CH_2O^{\bullet} + H_2 \text{ ----------(2)}$$

$$CH_3CH_2OH + H^{\bullet} \longrightarrow \dot{C}H_2CH_2OH + H_2 \text{ ----------(3)}$$

When organic halides are irradiated, the general observation has been that iodides form iodine, bromides tend to form hydrogen bromide in addition to bromine, and chlorides form hydrogen chloride and no free chlorine[38]. The products also include alkanes and alkenes. Isomerisation effects have been reported by Wiley et al.[39] in the radiolysis of chlorinated alkanes; for example, irradiation of propyl chloride afforded isopropyl chloride and 1,3- dichloropropane gave 1,2- dichloropropane.

Radiation readily causes polymerisation of reactive monomers and Schmitz and Lawton[40] studied the polymerisation of acrylates, methacrylates, styrene and acrylonitrile by X-rays. They observed that the reactions were inhibited by the presence of oxygen or benzoquinone as expected for free

radical reactions. However the results of Davison et al.[41] on the action of gamma-rays and electrons on isobutene are consistent with an ionic mechanism for the radiation induced polymerisation.

Many chemical and physical effects are observed when polymers themselves are irradiated. Main chain and side chain degradation of polymethacrylate has been observed by Alexander et al.[42]. In particular they have studied the effects of radiation on polythene. After small doses of radiation many disadvantages, which are present before radiation treatment, are partially overcome. The crosslinked polythene is no longer soluble in any organic solvents, and at 120°C, instead of melting to form a viscous liquid, it merely softens and forms a rubber-like material.

Finally it is worth mentioning that many radiation induced decompositions have been followed by the use of radical scavengers. Owing to the phenomenon of indirect action, the change brought about in any solute which is an efficient radical "catcher", may be used as a measure of the yield of radicals from the irradiation of the solvent. For example Prevôt-Bérnas et al.[43] have followed the radiation induced decomposition of carbon tetrachloride by the use of the radical scavenger diphenyl picryl hydrazyl (D.P.P.H.). Vinyl Monomers[44] and iodine[45] have also been used as radical catchers.

The Present Work

In the work about to be described carbon tetrachloride was the first compound to be irradiated with gamma-rays. The nature of the products viz. chlorine and hexachlorethane then suggested the irradiation of solutions of the aromatic hydrocarbons, benzene and toluene in carbon tetrachloride in order to study the attack of the trichloromethyl radical and the chlorine atom on the aromatic ring.

FIGURE I

APPARATUS USED IN THE COBALT-60 IRRADIATION CHAMBER

DIAGRAM I

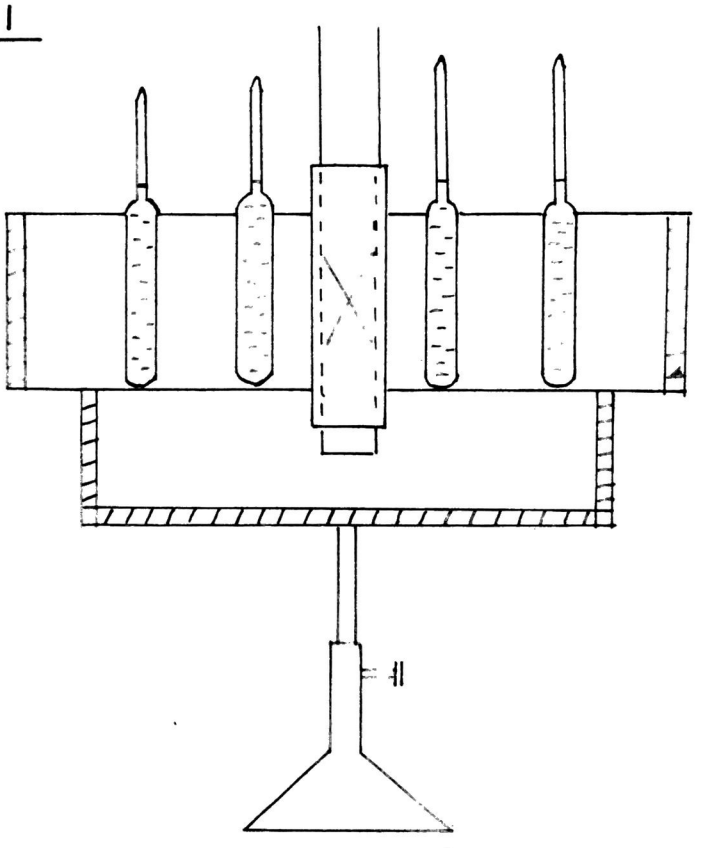


DIAGRAM II

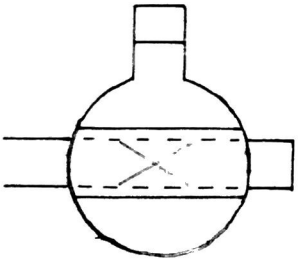
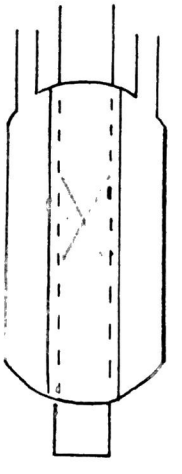


DIAGRAM III



Similarly, pure solutions of chloroform and methylene chloride were irradiated.

The unsaturated compounds, vinylidene chloride, allyl chloride, tetrachlorethylene and hexa chlorobutadiene were irradiated in order to illustrate differences which are observed in the radiolysis of saturated and unsaturated chlorinated compounds.

Allyl chloride was polymerised readily by gamma-rays and the extent of the contribution made to the polymerisation by the breaking of the carbon-halogen bond was determined by irradiating allyl bromide and allyl iodide under the same conditions.

Some unpublished results obtained by other radiation workers here in this department will be considered for comparison purposes viz. the irradiation of carbon tetrachloride - para xylene mixtures[46]; the irradiation of cis and trans dichlorethylene and trichlorethylene[47] and the irradiation of allyl fluoride and allyl bromide[48].

Techniques

The radiation unit used in this work was set up in 1954 in conjunction with A.E.R.E., Harwell, being rather similar in design and operation to that described by Gibson and Pearce[49]. A cobalt-60 source of 102 Curies was installed in 1954, and replaced in March 1957 by a 140 Curie source and a 64 Curie source. The sources were available in the form of single rods, which could be withdrawn by electric motor into a concrete block, then returned to the same position in the radiation chamber as required.

Solutions for which no rigorous precautions were taken to exclude air were irradiated in annular Pyrex glass vessels fitted with glass stoppers, of capacity 50 mls to 2000 mls (figure 1, diagrams II and III).

On the other hand, solutions in vacuum were irradiated in sealed Pyrex glass tubes of capacity 80 mls. It was possible to irradiate 16 of these tubes at the one time by placing them in fixed positions in an inner and an outer circle on a metal stand with the source at the centre (figure 1, diagram I).

It was confirmed experimentally that the same amount of radiation was received by each individual tube in each of the two circles.

All irradiation vessels, before being filled with a pure solution, were left for 24 hours in a chromic acid bath, thoroughly rinsed with distilled water, and dried in an electric oven for 2 hours.

Dosimetry

For quantitative results it is necessary to measure the energy absorbed in a solution on exposure for a given time to a source of ionising radiation.

The units of absorbed energy used in this work are the roentgen (r) and the electron volt (eV). In water the energy absorption corresponding to 1r is 93 ergs per m.l. for all radiations above about 50 keV. 1eV is equivalent to 1.60×10^{-12} ergs. The term "dose-rate" is used to denote the rate of energy absorption, which can be expressed, for example, in roentgens per unit time per unit volume of absorbing medium, e.g. r/c.c./min. Dose-rate can also be expressed, for example, in electron volts (eV) per unit time per unit volume, e.g. eV/c.c./min.

Owing to the involved techniques of the physical measurement of absorbed energy, it has become common practice in radiation chemistry to use for measurement of dose, a radiation-induced chemical reaction, whose dependence on dose has previously been studied. That most commonly employed

is the oxidation of ferrous sulphate in aerated aqueous solutions 0.5 to 1N with respect to sulphuric acid[50, 51].

The chemical yield of this oxidation has been measured accurately by spectrophotometric measurements, and the energy input has been measured by calorimetry [52, 53] and ionization chamber methods[54]. These results are in good agreement on a value of 15.5 $\pm$ 0.2 ferric ions produced per 100 electron volts absorbed in the solution[51]. Thus ferrous ions are oxidised in 0.5 to 1N sulphuric acid, with a G-value of 15.5 $\pm$ 0.2

The ferrous sulphate or "Fricke" dosimeter, as it is sometimes called, has some disadvantages in certain conditions. For example, for total doses of less than 2000r, the ferrous system is not sensitive enough, and although certain chain reacting systems have been proposed[55], their use is probably precluded by the lack of a linear relation between response and dose rate. Also for doses greater than 50,000r of gamma-radiation, air saturated solutions become depleted of oxygen if irradiated in a closed system, and the ferric yield falls[50], whereas the reduction of ceric ions proceeds smoothly to much higher doses.[56]

Some physical changes have also been considered as dosimeters, such as the colouration of certain glasses[57] and the luminescence of phosphors.[58] Pyrex glass upon irradiation assumes an intense brown colouration ascribed to the production of absorption bands when electrons are trapped by lattice imperfections or impurity atoms.

Since the absorption of gamma-rays takes place predominantly by Compton scattering, it follows that the energy absorption by any given medium will be directly proportional to the "electron density" of that medium. Consequently a correction must be made for this when comparing the energy

absorbed by some other solution with that absorbed by the ferrous sulphate solution.

$$\text{Energy absorbed by other solution} = \text{Energy absorbed by ferrous solution} \times \frac{\text{electron density of other solution}}{\text{electron density of ferrous solution}}$$

where the electron density (N_e) of 1 ml. of liquid is given as:

$$N_e = \frac{P}{M} \times N \times \sum Z$$

where P = density of the liquid

M = Molecular weight of the liquid

N = Avogadro's number

$\sum Z$ = Sum of the atomic numbers of the different elements in the molecule of the liquid

The electron density of the ferrous solution is obtained by treating it as pure water with density = 1.023 gms/cc.

Experimental determination of dose rate

Reagents required

1) Analar Ferrous Ammonium Sulphate $FeSO_4 (NH_4)_2 SO_4, 6 H_2O$.

2) Analar Sulphuric Acid

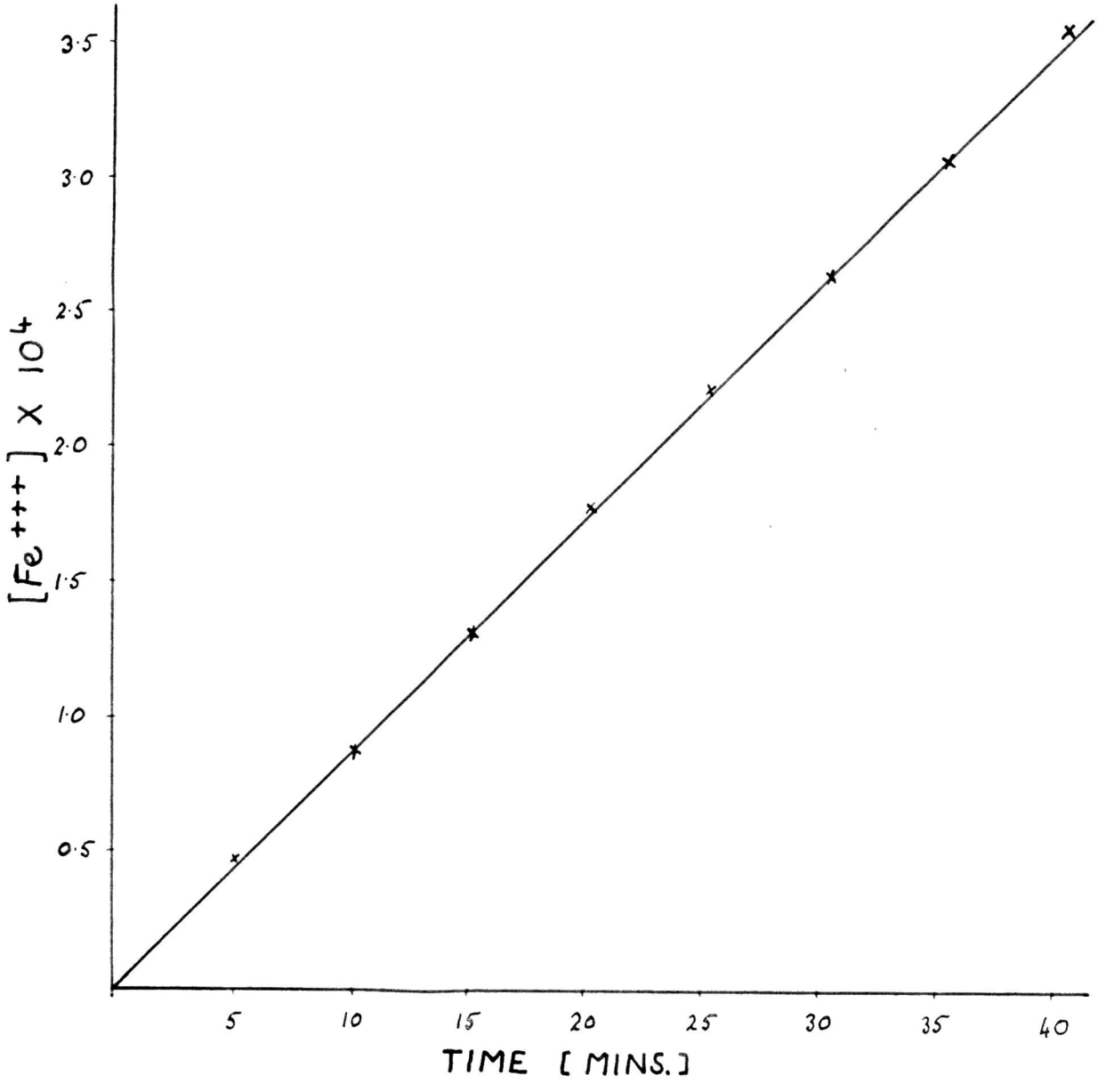
3) Pure water free from organic impurities. Triple distilled water was used i.e. distilled once from acid dichromate solution, then from aqueous potassium carbonate, and finally distilled once without any reagent present.

1 litre of $\frac{M}{100}$ ferrous ammonium sulphate solution 0.8 $\bar{N}$ with respect to sulphuric acid was prepared with pure water. A previously cleaned and dried irradiation vessel was filled with ferrous solution and placed at the cobalt-60 source in a definite position marked on the source tube. Samples of solution were removed at 5 minute intervals, and the ferric ion concentration was measured spectrophotometrically with a Unicam S.P. 500 by comparing the transmission of light of the irradiated sample, with that of the original ferrous solution. The molar extinction coefficient of ferric

FIGURE 2

DOSE RATE DETERMINATION

CONCENTRATION OF FERRIC IONS PRODUCED BY GAMMA - RADIATION.



ions in 0.8 $\bar{N}$ sulphuric acid at 304 mμ is known (table 1), and the ferric ion concentration was calculated from:

$$\log \frac{Io}{I} = e\ c\ d$$

where: e = molar extinction coefficient

c = concentration in moles per litre

d = cell thickness (cms).

A typical determination for tubes placed in the inner circle of the metal stand is given in table 2, and the results are graphed in figure 2. From the graph:

$$\frac{d\ (Fe^{+++})}{dt} = 8.279 \times 10^{-6} \text{ moles/litre/min.}$$

$$= 8.279 \times 10^{-9} \times 6.025 \times 10^{23} \text{ atoms/cc/min}$$

Now in the system $Fe^{++} \longrightarrow Fe^{+++}$ G = 15.5 molecules/100 eV

∴ Energy absorption of the ferrous solution in the glass tube $= \frac{8.279 \times 6.025 \times 10^{14} \times 10^{2}}{15.5}$ eV/cc/min

i.e. Dose rate $= 3.22 \times 10^{16}$ eV/cc/min

Now 1eV ≡ 1.602×10^{-12} ergs

and 1r ≡ 93 ergs

∴ Energy absorption of the ferrous solution in the glass tube $= \frac{3.22 \times 10^{16} \times 1.602 \times 10^{-12}}{93}$ r/cc/min

i.e. Dose Rate = 554 r/cc/min

Supposing **x** moles of organic product were formed per cc per minute from the irradiation of a similar volume of organic solution in a tube in the inner ring, with the metal stand occupying the same position on the source, then:

Energy absorption of the organic solution $= 3.22 \times 10^{16} \times \frac{Ne\ (\text{organic solution})}{Ne\ (\text{ferrous solution})}$ eV/cc/min

$= E$

$\therefore$ G (organic product) $= \frac{100 \times N}{E}$ N: Avogardro's number

Below are listed typical dose rates for different irradiation vessels.

60 - Curie source	140 - Curie Source
556 ml vessel - 586 r/cc/min.	55 ml vessel - 1950 r/cc/min
940 ml vessel - 530 r/cc/min.	395 ml vessel - 1670 r/cc/min.
2140 ml vessel - 460 r/cc/min.	

Table 1.

The molar extinction coefficient for ferric ions in 0.8 N sulphuric acid solution at 304 mu.

T°C	e
15	2074
16	2089
17	2104
18	2119
19	2135
20	2150
21	2165
22	2181
23	2197
24	2213
25	2229

e : molar extinction coefficient at a temperature of T°C.

Table 2

Dose Rate Determination : Concentration of Ferric ions produced by γ - irradition

Time (mins)	$\log I_o/I$	Temperature ^oC	(Fe^{+++}) moles x 10^4
5	0.082	20	0.4801
10	0.175	20	0.8139
15	0.267	20	1.242
20	0.359	20	1.670
25	0.460	20	2.140
30	0.546	21	2.522
35	0.640	22	2.934
41	0.758	22	3.475

Gas-Phase Chromatography (G.P.C.)

At the outset of the work it was realised that a highly sensitive analytical technique would have to be developed to allow analysis, qualitative and quantitative, of irradiation products which were expected in many reactions to be present in very minute amounts. Accordingly several gas-phase chromatography units of conventional design were constructed. These units gave reliable results for the following systems:

(i) Methyl chloride and methylene chloride in chloroform.

(ii) Chloroform in carbon tetrachloride and vice versa.

(iii) Impurities in carbon tetrachloride, chloroform, methylene chloride, toluene and benzene.

(iv) Benzyl chloride and chloro-toluenes in toluene-carbon tetrachloride mixtures.

(v) Chlorobenzene in benzene-carbon tetrachloride mixtures.

Unsatisfactory results were obtained in the case of high-boiling compounds such as hexa chlorethane, hexa chlorobutadiene, benzal chloride, benzotrichloride, p-methyl benzal chloride, p - methyl benzotrichloride, benzyl chloroform, diphenyl, dibenzyl etc. Either (a) the materials were not eluted or (b) the column conditions required - a high temperature and a low liquid content in the packing - limited the efficiency of separation and the life of the column. The latter is important if a long series of related analyses is required. It was concluded that the straight forward extrapolation of low-temperature techniques to higher temperatures was futile. This problem was tackled in two ways.

The first approach was the study of gas-solid adsorption chromatography. The common solids used in adsorption chromatography e.g.

alumina, charcoal, magnesium oxide, are stable over a large temperature range and no problem arises due to decomposition. Using alumina as a solid phase, a technique was developed dependent on four essential conditions:

(i) Flash vaporisation of the analytical sample.

(ii) The use of the minimum length of column.

(iii) The use of the lowest possible column temperature.

(iv) The maintenance of a high exit temperature between the column and the flame detector to avoid condensation.

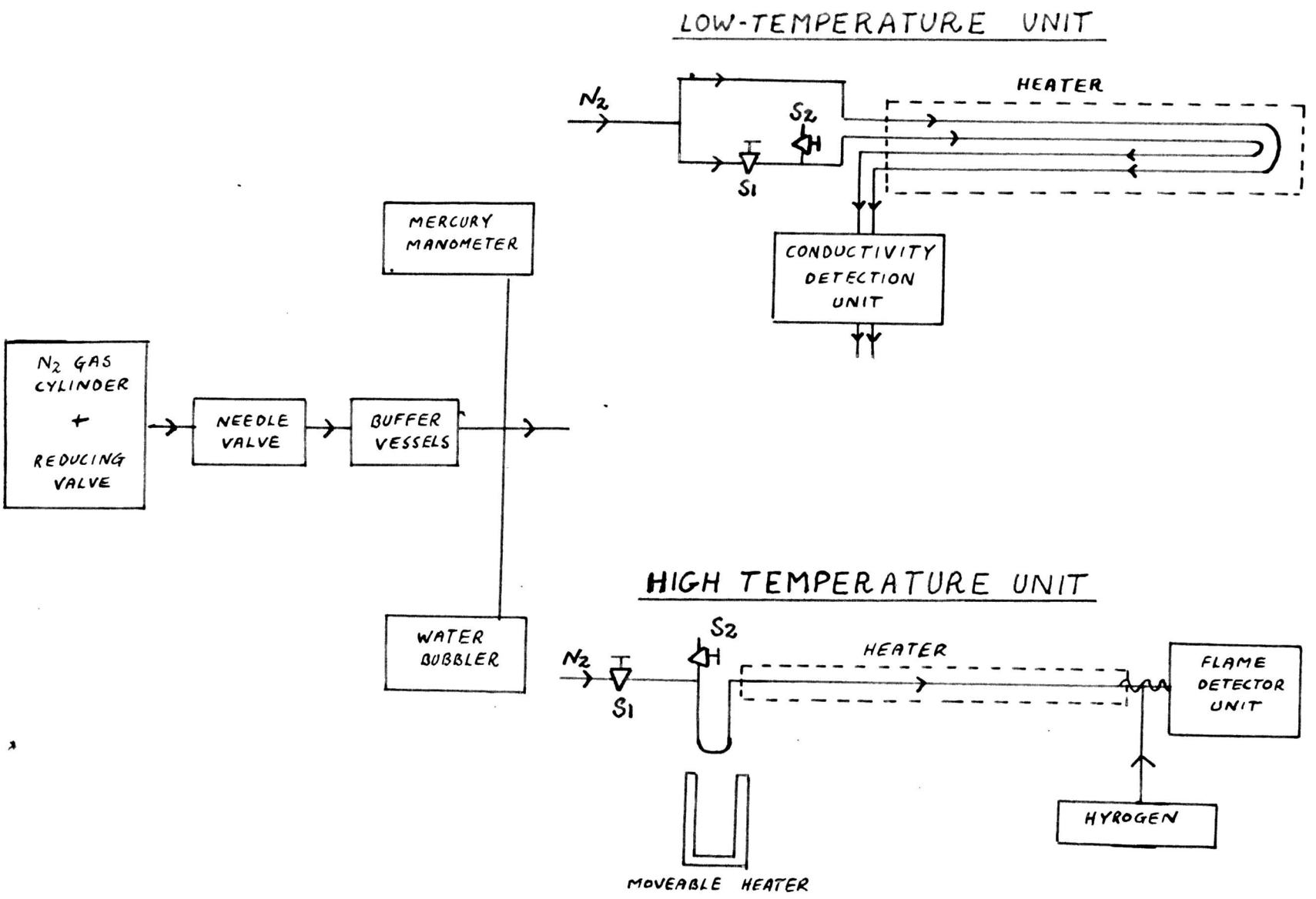
Successful separations of stable substances such as hydrocarbons e.g. diphenyl, stilbene and dibenzyl, and aromatic halogeno compounds e.g. p-chloro toluene and benzyl chloride were achieved. Many of these proved to be applicable to systems under examination but the most urgent problem remained unsolved. Unstable halogeno compounds were decomposed at high temperatures and no analyses of substances such as benzotrichloride, p-methyl benzotrichloride etc., were possible.

The second programme developed from the application of the four essential conditions already listed to gas-liquid chromatography. Using an extremely short column of a standard silicone oil - Celite packing with flash vaporisation and the maintenance of a high outlet temperature, separations were achieved at column temperatures below 140°C of compounds with boiling points up to 250°C. Apparently the low temperature increased the separation factor far in excess of the loss incurred by shortening the column.

By the use of this column technique many efficient measurements of separated products were made, notably hexachlorethane in reaction mixtures. The power of the method is revealed in the case of the products from an

FIGURE 3

GAS PHASE CHROMATOGRAPHY UNITS



irradiated toluene-carbon tetrachloride solution. The separated products included the following: (i) hexachlorethane, (ii) benzyl chloride, (iii) chloro-toluenes, (iv) methyl benzal chloride, (v) methyl benzotrichloride benzyl chloroform, (vii) a mixture of hydrocarbons, mainly dibenzyl, but also probably para-benzyl toluene and stilbene.

Description of the apparatus

Only a brief description of the apparatus and its mode of use will be given for in recent years, gas phase chromatography has become a commonplace analytical tool and several excellent reviews have been published on the subject[59].

The principal components of the different units are shown in figure 3.

Each unit required a well-buffered flow of oxygen-free nitrogen and the high temperature unit also required a similarly regulated flow of hydrogen. A steady flow was maintained from the cylinders by means of a reducing valve, a needle valve and a number of glass buffer vessels placed in series. The water bubbler acted as a safety valve.

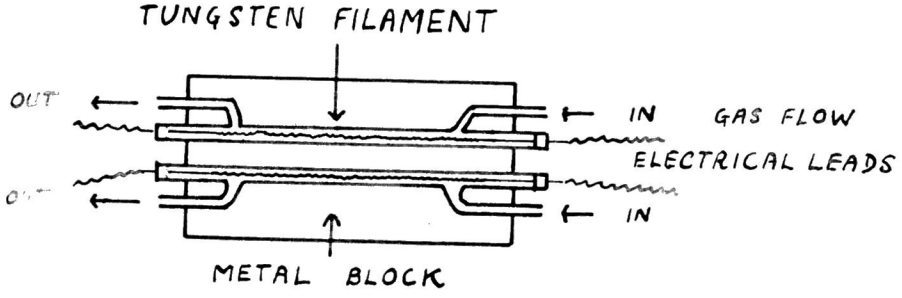
The injection system consisted simply of a stopcock S1 to cut off the nitrogen flow and a stopcock S2 through which the sample to be analysed was introduced using an Agla micrometer syringe. A moveable heating jacket was used to vapourise the injected sample in the high temperature unit.

In the conventional low temperature unit the chromatograph columns were in the form of Pyrex glass U-tubes of internal diameter 6-8 m.m. and total length 150-180 cms. The columns were kept at a steady temperature in the range 60-90°C inside a well-lagged heater made by winding resistance tape on a glass tube and feeding a current through the tape from a Claude-Lyons variac transformer. Adequate temperature control ($\pm$ 2°C at 80°C) was obtained in this way.

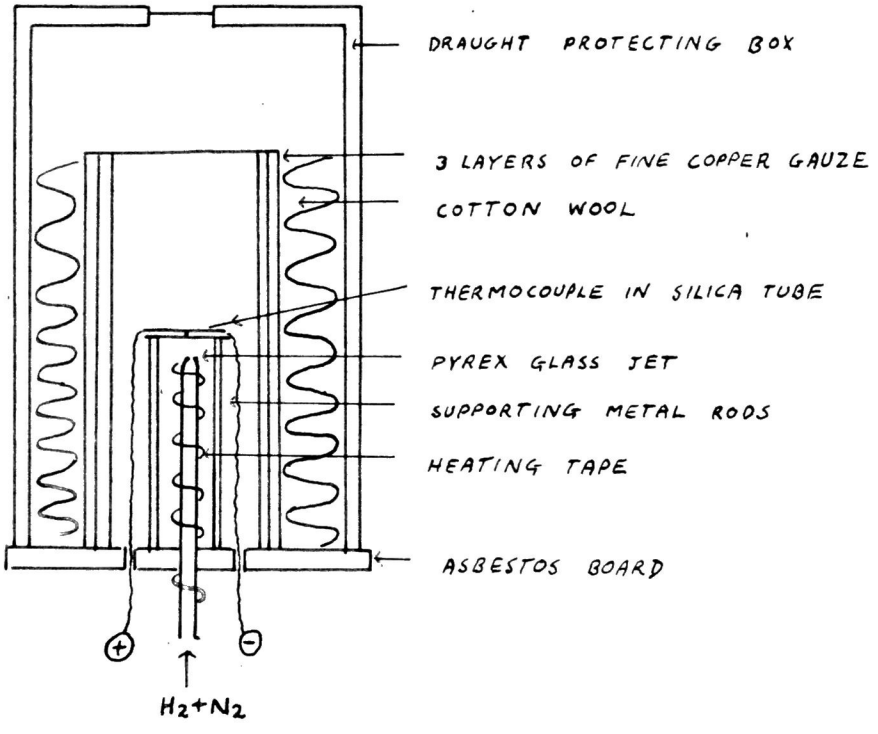
FIGURE 4

GAS CHROMATOGRAPHY DETECTION UNITS

(i) THERMAL CONDUCTIVITY BLOCK



(ii) HYDROGEN FLAME DETECTOR UNIT



The column packings were varied considerably. The most commonly used stationary oil phases were B.D.H. Tricresyl Phosphate, B.D.H. Squalane and Hopkin and Williams silicone fluid M.S. 500. 20-25% by weight of these oils were absorbed on to Johns-Manville Celite 545 (mesh 25-80) or on to Fosal Sil (mesh 25-80).

In the high temperature unit the chromatograph columns were straight glass tubes of internal diameter 6-8 m.m. and total length 30-40 cms. The heater was similar to that already described. It was important in this unit that the moveable heating jacket, acting as a flash vapouriser, and the exit tube between the column heater and the flame jet were maintained at a temperature above the boiling point of the injected sample.

Only one packing was used in the high temperature column i.e. 30% by weight of silicone oil absorbed on to unmeshed Celite. This mixture was packed in the column to give a flow rate of approximately 60 mls/min of nitrogen when the inlet pressure of nitrogen was 20 cms. Hg above atmospheric pressure.

The katharometer detection unit shown in figure 4 was in the form of a metal block suitably drilled with two stretched tungsten filaments placed in the gas streams through the block. The filaments formed two arms of a Wheatstone bridge network (figure 5); current to the bridge being supplied by a 4 volt battery. The out of balance e.m.f. was measured on a 0.5 milli-volt full scale deflection Sunvic recorder. The sensitivity of the apparatus was controlled by altering the bridge current by means of a variable resistance in series with the battery.

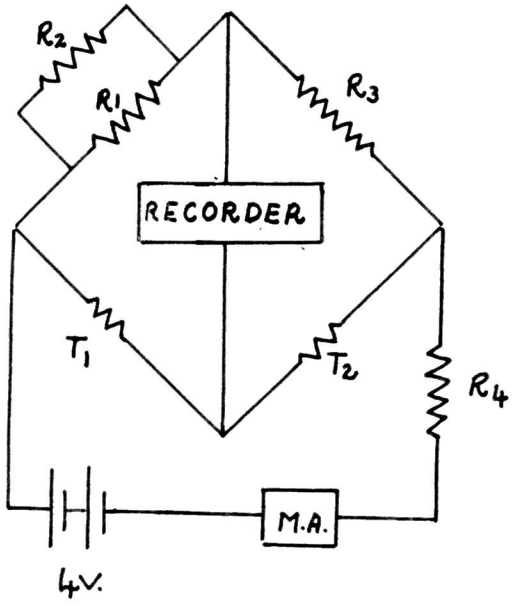
The detector in the high temperature apparatus was an iron alloy thermocouple supported in a protecting silica capillary at a height of 0.5 cm.

FIGURE 5

GAS CHROMATOGRAPHY ELECTRICAL CIRCUITS

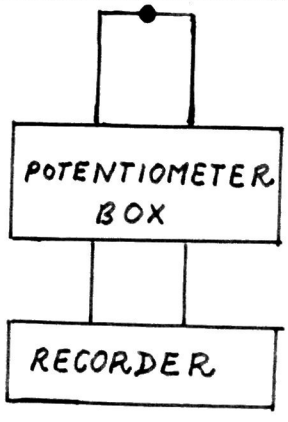
(i) THERMAL CONDUCTIVITY GAUGES

R : VARIABLE RESISTANCES
T : TUNGSTEN FILAMENTS



(ii) THERMOCOUPLE UNIT

IRON ALLOY THERMOCOUPLE



above a 0.5 m.m. diameter Pyrex glass jet. Several layers of fine copper gauze, cotton wool packing and a large cardboard box protected the small hydrogen flame from draughts (figure 4). The electrical circuit is shown in (figure 5) where again the out of balance e.m.f. was fed to an automatic Sunvic recorder.

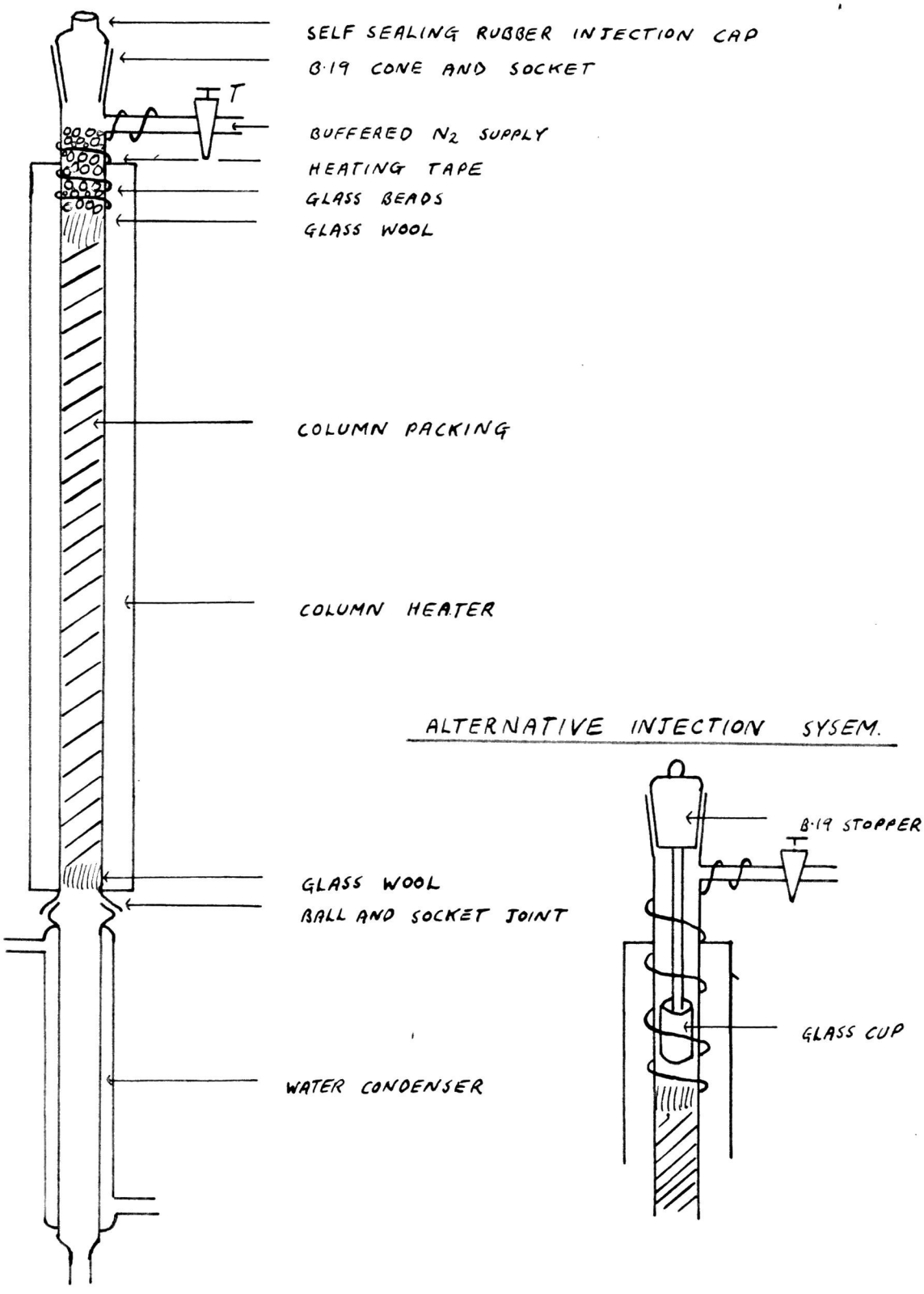
When the low temperature apparatus was operating at maximum sensitivity it was possible to detect quite readily 0.05% chloroform in carbon tetrachloride in a 0.01 ml. injection. The sensitivity of the high temperature unit was very dependent on the nature of the compounds being detected. For example in 0.01 ml injections it was possible to detect 0.4% para-chloro toluene in toluene but only 1.5% hexachlorethane in carbon tetrachloride was detected. Accurate quantitative estimations of the components in a mixture were obtained by injecting samples from prepared standards until a duplication of peaks was obtained. This method was adopted rather than the measurement of peak heights or peak areas, to reduce the errors due to normal temperature and pressure fluctuations.

Large scale gas phase chromatography separation unit

In addition to the apparatus already described a large scale G.P.C. separation unit was erected. A 1-2 gm sample of a mixture was injected on this column and the separate fractions as they emerged from the column were condensed in a water condenser. In many cases a little ether was used to wash the fraction into a receiving vessel. By repeated injections of the same mixture fractions were built up until gram quantities were obtained on which physical and chemical tests were carried out. Fractions were collected at 2-3 minute intervals by the use of two separate water condensers. The composition of each collected fraction was then determined by injecting a

FIGURE 6

LARGE SCALE G.P.C. SEPARATION UNIT



0.01 ml sample into the small scale G.P.C. unit.

Details of a typical separation are given in table 3. The technique has also proved successful in the separation of products from the irradiation of benzene-carbon tetra-chloride and toluene-carbon tetrachloride mixtures. Cis and trans isomeric dimers from the irradiation of 1, 2-dichlorethylene have also been separated in this way.

Description of the apparatus

The carrier gas was a buffered flow of oxygen-free nitrogen from a cylinder. This was led through tap T (figure 6) into a Pyrex glass column, 12-14 mm. diameter and 36 cms. in length, and surrounded by a column heater whose temperature was varied between 90-120°C. The column packing was 30% Silicone oil absorbed on to unmeshed celite.

The sample was injected with a syringe through a self-sealing rubber cap on to a layer of heated glass beads which acted as a flash vapouriser. The temperature at this part of the column was kept above the boiling point of the injected sample. An alternative injection system for the introduction of solid mixtures or very viscous oils consisted of a Pyrex glass cup attached by a length of glass rod to a B.19 stopper, (figure 6). The sample after being placed in the cup was immediately vapourised when the cup was replaced in the preheated part of the column.

Table 3.

A separation of some of the products from the irradiation of chloroform

Column packing	:	30% Silicone oil - Celite
Column temperature	:	105°C
Vapouriser temperature	:	200°C
Nitrogen flow rate	:	85 mls/min.

Time	% Composition of fraction collected		
(mins.)	sym-$C_2H_2Cl_4$	C_2HCl_5	C_2Cl_6
	bp 146°C	bp 162°C	bp 185°C
7	100	-	-
9	30	70	-
11	5	95	-
13	-	98	2
15	-	95	5
17	-	80	20
20	-	25	75
25	-	5	95

30 - 50 C_2Cl_6 contaminated with a very thin film of viscous oil.

The use of Alumina as a column packing in the large scale gas phase chromatograph unit

Certain compounds such as diphenyl, dibenzyl and the isomeric hexa-chloro-cyclo-hexanes were only eluted from a silicone oil - Celite packing at high temperatures, use of which caused the stationary oil-phase to flow, so destroying the uniformity of the packing. Therefore alumina was used as the column packing at a temperature of 400°C. Some remarkable results were obtained with this agent. Many compounds decomposed on the column at this temperature and the collected fractions represented the decomposition products.

The aromatic hydrocarbons came off the column unchanged. However, keto substituted aromatic compounds such as tetralone underwent dehydration on the column and crystals of naphthalene were collected in the water condenser. The hexa-chloro-cyclo hexane isomers were converted on the column by a halogenolysis reactions to a mixture of the tri-chloro benzenes containing 90% of the 1,2,4-isomer.

A complex reaction occurred when acetone was introduced into the column. The separated products included mesitylene, mesityl oxide, phorone and hydroxy and methyl substituted aromatic compounds as the major products.

Even more interesting results were obtained when a 2 inch plug of palladised charcoal was placed at the top of the alumina packing. Dehydrogenation reactions then occurred. For example tetralin and decalin were converted to naphthalene and acenaphthene was converted to acenaphthylene. Many dihydro and tetra hydro compounds were dehydrogenated to the corresponding unsaturated hydrocarbon in this way, and in many cases, dehydration and dehydrogenation reactions occurred simultaneously. For example tetra-hydro-keto-fluoranthene was completely converted to fluoranthene in 10 minutes.

Only a very brief description has been given of this section of the work using the large scale G.P.C. unit because many of the reactions and decompositions studied were irrelevant to the main course of the work. However, the examples given illustrate the potential of the method as a very useful tool in organic chemistry.

General Experimental Details

Infra-red spectra : from a Hilger H.800 double-beam infra-red spectrometer equipped with a sodium chloride prism.

Ultra-violet spectra : from a Unicam S.P. 500.

Refractive indices : from an Abbé refractometer kept at a constant temperature of 20°C.

Chemical analyses : from D.G. Weiler and F.B. Strauss in Oxford.

X-ray powder photographs : obtained in this department by courtesy of Dr. C.A. Beevers. All photographs obtained will be found in the appendix.

S E C T I O N I

The Irradiation of the Chlorinated Methanes:

Carbon tetrachloride, chloroform and methylene chloride.

INTRODUCTION

Early workers studied the photochemical decomposition of carbon tetrachloride and chloroform by ultra-violet light, and Baskerville[60], in 1912, reviewed this field. The main products reported were chlorine gas, hydrogen chloride and hexachlorethane. Since then, other workers[61], studying the photochemical decomposition of chloroform in the presence of air or oxygen, have reported the presence of chlorine, hydrogen chloride, phosgene, water, carbon dioxide, hexachlorethane and various peroxides. Carbon tetrachloride under the same conditions has been observed to give chlorine, phosgene and hexachlorethane, and no peroxide, possibly because there are no hydrogen atoms available[5].

The first worker to report a study of the decomposition of carbon tetrachloride and chloroform by ionising radiation was Kailan[62], in 1917. He noted that chlorine gas, hydrogen chloride and hexachlorethane were produced from chloroform by the action of the mixed gamma and beta-rays from radium. These results were confirmed later by Bishop[63] in 1933, and Harker[64] in 1934, using gamma and X-rays.

Cronheim and Gunther[65], in 1930, irradiated dry and oxygen-free chloroform and carbon tetrachloride with X-rays, and they noted the main products hydrogen chloride and chlorine respectively. They observed that the amount of hydrogen chloride generated was proportional to the X-ray energy absorbed, and they attributed the hydrogen chloride production in chloroform to a chain reaction of the type:

$$Cl^{\bullet} + CHCl_3 \longrightarrow CCl_3^{\bullet} + HCl$$

$$CCl_3^{\bullet} + CHCl_3 \longrightarrow Cl^{\bullet} + CCl_3CHCl_2$$

Although the early workers studying the decomposition of carbon

tetrachloride and chloroform by ionising radiation all reported the same products, there was wide divergence in the yields of products reported. This is not surprising if one attributes these discrepancies to impurities present in the samples they used, for recent workers have shown that the effect of impurities is extremely marked, a characteristic of a chain reaction.

Schulte et al.[66], in 1953, examined the chemical effects produced in chloroform in the presence of oxygen by gamma rays, and claimed that reproducible data could only be obtained by using chloroform which had been subjected to a very thorough purification procedure. They observed that the effect of oxygen on the reaction was striking, the chloroform being oxidised by a chain mechanism to give a peroxide as the primary product.

$$CHCl_3 + O_2 \longrightarrow CCl_3OOH$$

As the reaction proceeds the peroxide disappears and the hydrogen chloride concentration builds up. It is of interest to note that these workers favour Kailan's original suggestion, in 1917, that the disappearance of the small quantity of chlorine produced in the early stages of the irradiation can be accounted for by the reaction:

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

Following that work, Schulte[67] then examined the chemical changes in carbon tetrachloride containing dissolved chlorine under the influence of gamma-rays. He observed two reactions viz. 1) the exchange of chlorine with carbon tetrachloride and 2) the decomposition of carbon tetrachloride to form chlorine and hexachlorethane. He found that the rates of both reactions were independent of the chlorine concentration, and directly proportional to the dose rate, and concluded that the former reaction could be taken as a measure of the radical yield in the system, while the latter reaction could

be interpreted as a measure of molecular yields.

In recent years, workers have favoured the use of radical scavengers to follow the radiation induced decomposition of carbon tetrachloride and chloroform. Prevôt-Bérnaset al.[43] followed spectrophotometrically the disappearance of the highly coloured diphenyl picryl hydrazyl (D.P.P.H.) in irradiated carbon tetrachloride and chloroform, as a measure of the number of free radicals formed. They observed a post-irradiation effect, the D.P.P.H. continuing to disappear after irradiation had ceased. They attributed the "after effect" to a relatively slow reaction, as compared with the free radical reaction, of hydrogen chloride and chlorine from chloroform and carbon tetrachloride respectively with D.P.P.H. To account for the formation of chlorine and hydrogen chloride in the presence of D.P.P.H. they postulate a number of ionic reactions e.g.

$$CCl_4 \longrightarrow Cl_2 + CCl_2^{++} + 2e$$

$$CHCl_3 \longrightarrow HCl + CCl_2^{++} + 2e$$

A slightly different technique was used by Schultz[68], who used the oxidising fragments from the radiolysis of chloroform and methylene chloride to produce the coloured form of crystal violet from the leuco base, the reaction again being followed spectrophotometrically.

Very different values for G (number of radicals formed) have been reported for the different techniques; this will be commented upon later.

The chemical effects observed from the gamma-ray induced decomposition of carbon tetrachloride, chloroform and methylene chloride will now be described.

EXPERIMENTAL

Preparation of pure dry carbon tetrachloride

Carbon tetrachloride, from May and Baker, was dried for several days with phosphorus pentoxide, filtered, and distilled immediately before use. The first and last 10% fractions of the distillate were discarded. Any dissolved phosgene was found in the first 10% of distillate.

N^{D}_{20} = 1.4606 (Literature N^{D}_{20} = 1.4605)

A G.P.C. analysis showed the presence of a very small peak before the main carbon tetrachloride peak representing 0.04% of chloroform as an impurity. A fractional distillation using a 4 ft. long, 1 inch diameter glass column packed with Stedman metal gauze rings, surrounded by an electrical heater, and attached to a stillhead with an adjustable take-off did not improve further the purity of the carbon tetrachloride.

Irradiation of carbon tetrachloride in the presence of dissolved air

A 55 ml. annular glass vessel was filled with the purified carbon tetrachloride, stoppered and irradiated at a dose rate of 1945 r/cc/min for 143 hours.

The irradiated solution was then pale-green in colour with a smell of phosgene evident; white fumes were obtained with concentrated ammonia vapour.

The solution was transferred to a weighed distillation flask and concentrated by a careful distillation, to remove carbon tetrachloride, to a final volume of approximately 8 mls. The flask was reweighed and the amount of hexachlorethane present in the concentrated irradiated carbon tetrachloride solution was determined by a G.P.C. analysis.

The remaining carbon tetrachloride was evaporated off slowly and the white crystalline irradiation product was purified by sublimation m.p. = 185 - 186°C (sealed tube). (Authentic hexachlorethane m.p. 187°C). A chemical analysis of the purified material was obtained.

Analysis found		Analysis calculated for C_2Cl_6	
C	10.0%	C	10.2
H	0.2%	Cl	89.8
Cl	90.1%		
Total	100.3		

The identity of the crystalline material was confirmed as hexachlorethane by a comparison of the X-ray powder photographs of the two compounds. No differences were observed.

In order to confirm that no hexachlorethane co-distilled during the distillation process, the amount of hexachlorethane determined by G.P.C. analysis was accurately weighed out and dissolved in 55 mls of pure carbon tetrachloride. The solution was then concentrated by a careful distillation to a volume of approximately 8 mls, and the concentration of hexachlorethane in this portion was determined by G.P.C. analysis and compared with the amount originally weighed out. Results:

Amount of hexachlorethane weighed out = 0.164 gms.

Amount present in the concentrated solution = 0.161 ± 0.004 gms.

The two figures are in good agreement indicating that the possibility of co-distillation during the concentration of the irradiated solution could be ruled out as a source of error.

The results are given in table 4. The chlorine concentration in carbon tetrachloride irradiated in the presence of air was not determined.

A typical calculation is shown below. 55 mls of solution irradiated for 143 hours at a dose rate of 11.30×10^{16} eV/cc/min produced 0.675 millimoles of hexachlorethane.

(M) N^{o} of molecules of hexachlorethane $= 0.675 \times 10^{-3} \times 6.025 \times 10^{23}$

Total dose received by 55 mls of solution $= (55 \times 143 \times 60 \times 11.30 \times 10^{16})$eV

$= 5.33 \times 10^{22}$ eV

(E) Energy absorbed by CCl_4 $= (5.33 \times 10^{22}) \times \frac{Ne\ (CCl_4)}{Ne\ (H_2O)}$

where $Ne\ (CCl_4) = 0.7668 \times (6.025 \times 10^{23})$ electrons/molecule.

$Ne\ (H_2O) = 0.5683 \times (6.025 \times 10^{23})$ electrons/molecule.

$$G\text{ - value} = \frac{M \times 100}{E}$$

$$= \frac{0.675 \times 10^{-3} \times 6.025 \times 10^{23} \times 0.5683 \times 100}{5.33 \times 10^{22} \times 0.7668}$$

$$= \underline{0.5654}$$

The mean of the four values listed in table 1 gives $G = 0.57 \pm 0.06$ for the formation of hexachlorethane from carbon tetrachloride irradiated in the presence of dissolved air for total doses in the range 15×10^{6} - 8×10^{6} r/cc.

Irradiation of carbon tetrachloride in the absence of air

The tube used was thoroughly dried by flaming it while it was attached to a vacuum line. It was then allowed to cool, removed from the vacuum line, filled with pure carbon tetrachloride and replaced on the vacuum line. A vacuum flask containing liquid nitrogen was placed around the tube, in order to solidify the solution before opening the vacuum line to the oil diffusion pump, which was capable of reducing the pressure to 10^{-6} mm. Hg. The solution was degassed by closing off the pump line, removing the liquid

nitrogen, and raising a beaker of cold water around the tube. This last procedure was found to be necessary to avoid cracking of the glass tube as the solid slowly liquified. When liquifaction was complete, the solution was again frozen and opened to the pump line. This entire procedure was repeated several times until degassing was complete. A pirani gauge was attached to the pump line and the increase in the pressure reading on this gauge, when the solidified sample was opened to the vacuum line, was useful for indicating the completeness of the degassing procedure. The tube was sealed off under vacuum when degassing was complete.

Two other tubes were filled with carbon tetrachloride in a similar manner, and irradiated on the inner ring of the metal stand previously described, at a dose rate of 3.46×10^{16} eV/cc/min for 209 hours.

In spite of the rigorous procedure adopted for the removal of dissolved air and water vapour, traces of phosgene were detected by smell when the irradiated tubes were opened to the atmosphere.

In order to determine the chlorine concentration the tip of the tube was broken off, the solution in the stoppered tube was well shaken, and a pipetted sample was removed and added to potassium iodide solution. The liberated iodine was titrated with deci-normal potassium thiosulphate to the starch end-point. It was assumed that the above reagents did not react with hexachlorethane dissolved in the irradiated solution.

The hexachlorethane concentration in the remaining irradiated solution was determined as described previously by G.P.C. analysis.

The results are listed in table 4, giving a mean of 0.88 ± 0.03 for G (C_2Cl_6) and G (Cl_2) = 0.85 for carbon tetrachloride irradiated in the absence of air for a total dose of approximately 7.5×10^6 r/cc.

The irradiation of chloroform

Preparation of pure chloroform

B.P. Chloroform from T. and H. Smith was dried for several days with phosphorus pentoxide, and immediately before use was distilled over the same reagent in the presence of a stream of dry oxygen-free nitrogen. The first and last 10% fractions of the distillate were discarded. N^{D}_{20} = 1.4459 (Literature N^{D}_{20} = 1.4455).

A G.P.C. analysis showed the presence of two impurities viz. a) less than 0.04% methylene chloride and b) a trace of an unidentified impurity.

The irradiation of chloroform in the presence of dissolved air

400 mls of chloroform were irradiated in a stoppered annular glass flask for 120 hours at a dose rate of 9.1×10^{16} eV/cc/min.

Much fuming occurred when the stoppers were removed after irradiation and white fumes were obtained with concentrated ammonia vapour. A direct injection of the irradiated solution into the G.P.C. apparatus showed the presence of methylene chloride and carbon tetrachloride as products, and enabled a quantitative estimation of these two products to be made.

The hydrogen chloride content of the irradiated solution was determined volumetrically by shaking pipetted portions of the irradiated solution with deci-normal sodium hydroxide. The alkali layer was then extracted several times with water and back titrated with deci-normal hydrochloric acid using bromo phenol blue as an indicator. The determination of hydrogen chloride depends on the assumption that the other products from irradiated chloroform are unaffected by deci-normal acid and alkali. The validity of this assumption has not yet been confirmed by control experiments.

The remaining organic solution was concentrated by a careful distillation to a volume of approximately 4 mls and a G.P.C. analysis gave a quantitative analysis of the following reaction products:

(i) tetrachlorethylene (ii) sym-tetrachlorethane

(iii) pentachlorethane (iv) hexachlorethane

In addition there were three peaks at higher elution times on the G.P.C. chromatogram. Injections of compounds such as heptachloropropane, heptachloropropene and hexachlorobutadiene, showed that the three peaks represented compounds having volatilities of the same order as the injected standards. The possible structure of these three additional products will be discussed later.

In order to obtain sufficient quantities of the products listed above to confirm identification by other means, rather than G.P.C. analysis alone, further quantities of chloroform were irradiated for long periods and the product fractions were combined together. No attempt was made to calculate yields. The unchanged chloroform was distilled off and the mixture of products was separated into three fractions by distillation under reduced pressure (approximately 60 mm. Hg) using a small Vigreux fractionating column. A G.P.C. analysis of each fraction indicated that the fractionation was not very efficient and therefore the last two fractions were combined together and separated by the large-scale G.P.C. unit, described on page into a number of separate fractions (volume $\sim$ 0.2 ml). The composition of each fraction (see table 3) was checked by a G.P.C. analysis of a 0.01 ml. sample. The refractive index of each of the fractions shown to be pure was compared with the literature refractive index of tetrachlorethane, and pentachlorethane respectively. In addition the boiling points of the two pure fractions were determined by the micro-capillary method[69]. The results are listed on the following page:

sym-tetrachlorethane fraction	N_{20}^{D} = 1.4940	(Lit. N_{20}^{D} = 1.4942)
	b.p. = 144-145°C	(Lit. b.p. = 146°C)
pentachlorethane fraction	N_{20}^{D} = 1.5029	(Lit. N_{20}^{D} = 1.5035)
	b.p. = 157-158°C	(Lit. b.p. = 161°C)

The pure hexachlorethane fraction was obtained as a white crystalline compound and its identity was checked by the procedures previously described (see page 33).

The last fraction obtained from the G.P.C. separation column was crystalline hexachlorethane, with a thin film of viscous oil probably representing the traces of higher boiling products mentioned previously.

The first fraction obtained from the fractional distillation of the irradiation reaction mixture was subjected to the same procedure as outlined above for the final two distillation fractions, in an attempt to obtain a pure fraction of tetrachlorethylene. This was unsuccessful and therefore the absolute identification of this product depends on G.P.C. analysis alone.

The results from the irradiation of chloroform in the presence of dissolved air are listed in table 5. The electron density of chloroform was calculated to be $0.7233 \times (6.025 \times 10^{16})$ electrons per molecule.

The irradiation of chloroform in the absence of air

The procedure for preparing sealed tubes of chloroform in the absence of air was similar to that described for carbon tetrachloride.

Two 79 ml. portions of chloroform in sealed tubes were irradiated for 209 hours at a dose rate of 3.46×10^{16} eV/cc/min., and the products were estimated as described for chloroform irradiated in the presence of air.

The results of the two determinations are given in Table 5.

The irradiation of chloroform-carbon tetrachloride solutions in the absence of air.

Tubes containing 10% and 50% (by volume) of chloroform in carbon tetrachloride were sealed off in vacuum as described previously.

In each case approximately 84 mls of solution were irradiated for 209 hours at a dose rate of 3.46×10^{16} eV/cc/min.

The results obtained from the irradiation of the two solutions are given on table 6. The electron densities calculated were:

N_e (10% $CHCl_3/CCl_4$) = $0.7297 \times (6.025 \times 10^{16})$ electrons per molecule

N_e (50% $CHCl_3/CCl_4$) = $0.7451 \times (6.025 \times 10^{16})$ electrons per molecule

The irradiation of 10% (by volume) solution of tetrachlorethylene in chloroform in the absence of air

B.D.H. tetrachlorethylene was purified by the method described on page 62.

78 mls of the 10% solution were irradiated in a sealed tube for 143 hours at a dose rate of 3.46×10^{16} eV/cc/min.

The results are given on table 7. The electron densities calculated were:

N_e (C_2Cl_4) = $0.7866 \times (6.025 \times 10^{16})$ electrons per molecule

N_e (10% $C_2Cl_4/CHCl_3$) = $0.7297 \times (6.025 \times 10^{16})$ electrons per molecule

The irradiation of methylene chloride

Preparation of pure methylene chloride

Methylene chloride from B.D.H. was washed with several portions of water to remove dissolved phosgene, dried for several days with phosphorus

pentoxide and distilled immediately before use in the presence of phosphorus pentoxide. The first and last 10% fractions of the distillate were discarded. N_{20}^{D} = 1.423 (Lit. N_{20}^{D} = 1.424).

A G.P.C. analysis showed the presence of approximately 0.08% chloroform present as an impurity.

The irradiation of methylene chloride in the presence of dissolved air

435 mls of the solution were irradiated in a stoppered Pyrex annular glass vessel at a dose rate of 8.41×10^{16} eV/cc/min for 110 hours.

Fuming occurred when the stoppers were removed at the end of the irradiation period, and a sweet-smelling gas was given off. A direct injection of the irradiated solution into the G.P.C. apparatus identified this product as methyl chloride. In an attempt to obtain a more concentrated solution of methyl chloride in methylene chloride, a low temperature fractional distillation on the irradiated solution was carried out. A silvered, vacuum jacketed, 2 ft. long 1 inch diameter glass column packed with Fenske glass rings was employed. The still-head containing a "cold finger" filled with a solid carbon dioxide - acetone mixture was attached to two receiving vessels immersed in the same freezing mixture contained in thermos flasks. The distillation technique as such was successful, but unfortunately the hydrogen chloride also ascended the distillation column and condensed in the cold receiving tubes with the methyl chloride (bpt - 24°C). A G.P.C. analysis on the collected distillate was not possible because hydrogen chloride was found to interfere with the analysis.

Time was not available to repeat this work but in future experiments it would probably be preferable to remove the hydrogen chloride and the methyl chloride from the irradiated solution by means of a stream of nitrogen, allowing the mixture of gases to bubble through a wash bottle containing aqueous potassium

carbonate to absorb the acid. The methyl chloride could be collected in a cold receiving vessel containing a known volume of pure methylene chloride, and its concentration would then be determined by a G.P.C. analysis.

The determination of methyl chloride in the original volume of irradiated methylene chloride was very inaccurate and the G-value listed in Table 6 probably represents a lower limit, rather than an absolute value.

Hydrogen chloride was determined volumetrically on samples removed from the irradiated solution. The remaining solution was concentrated by distillation, and the following products were identified by a G.P.C. analysis of the concentrated irradiated solution:

(i) sym-dichlorethane (ii) 1, 1, 2 - trichlorethane

(iii) sym-tetrachlorethane

In addition four other peaks were detected on the G.P.C. chromatogram, corresponding to small amounts of higher boiling products. Their importance will be discussed later.

No other means were adopted for the identification of the products (i), (ii), (iii) above since insufficient reaction mixture was available for a separation into pure fractions by the G.P.C. separation method.

The results are listed in table 8 and must be regarded with some reservation as only one irradiation was carried out. The electron density of methylene chloride was calculated as:

$$N_e(CH_2Cl_2) = 0.6604 \times (6.025 \times 10^{23}) \text{ electrons per molecule.}$$

The irradiation of methylene chloride in the absence of air

78.5 mls of solution were irradiated in a sealed tube for 209 hours at a dose rate of 3.46×10^{16} eV/cc/min and the products identified and

estimated as described before.

The results are listed in table 8 and again must be regarded with reservation.

Table 4.

Results from the irradiation of carbon tetrachloride

a) In the presence of dissolved air

Volume irradiated mls	Irradiation time hours	Dose Rate eV/cc/min x 10^{-16}	Product C_2Cl_6 moles x 10^4	G - value C_2Cl_6
55	143	11.30	6.75	0.57
55	130	11.30	5.88	0.54
47	81	11.54	3.13	0.53
47	74	11.54	3.39	0.63

b) In the absence of air

All radiations were at a dose rate of 3.46 x 10^{16} eV/cc/min for 209 hours.

Volume irradiated mls	Product C_2Cl_6 moles x 10^4	G - values C_2Cl_6	Product Cl_2 moles x 10^4	G - value Cl_2
77	6.80	0.91	not determined	-
78	6.66	0.88	6.49	0.85
78	6.52	0.86	6.48	0.85

Table 5.

Results from the irradiation of chloroform.

	In the presence of dissolved air		In the absence of air	
Volume irradiated Dose rate Irradiation time	395 mls 9.1×10^{16} eV/cc/min 118 hours		Two determinations 79 mls 3.46×10^{16} eV/cc/min 209 hours	
Product	Moles of product $\times 10^4$	G - value	Moles of product $\times 10^4$	G - value
HCl	31.16	5.82	31.43 30.48	4.34 4.21
CCl_4	trace	< 0.1	trace trace	- -
CH_2Cl_2	6.203	1.16	9.559 9.993	1.32 1.38
sym - $C_2H_2Cl_4$	2.119	0.39	4.200 3.983	0.58 0.55
C_2HCl_5	4.136	0.77	6.806 7.168	0.94 0.99
C_2Cl_6	10.81	2.02	17.52 16.94	2.42 2.34
C_2Cl_4	0.5471	0.10	0.7964 1.014	0.11 0.14

Table 6.

Results from the irradiation of chloroform - carbon tetrachloride solutions in the absence of air.

	10% chloroform in carbon tetrachloride		50% chloroform in carbon tetrachloride	
Volume irradiated	84 mls		83 mls	
Dose Rate	3.46×10^{16} eV/cc/min		3.46×10^{16} eV/cc/min	
Irradiation time	209 hours		209 hours	
Product	Moles of product $\times 10^4$	G - value	Moles of product $\times 10^4$	G - value
HCl	33.29	4.10	35.58	4.53
CH_2Cl_2	0	0	not determined	-
sym - $C_2H_2Cl_4$	0	0	1.489	0.19
C_2HCl_5	trace	< 0.1	2.979	0.38
C_2Cl_6	25.97	3.20	21.24	2.71

Table 7.

Results from the irradiation of a 10% (by volume) tetrachlorethylene - chloroform solution.

Volume irradiated	78 mls	
Dose Rate	3.46×10^{16} eV/cc/min	
Irradiation time	143 hours	
Product	Moles of Product $\times 10^4$	G - value
HCl	13.92	2.82
CCl_4	0	0
CH_2Cl_2	not determined	-
sym - $C_2H_2Cl_4$	1.974	0.40
C_2HCl_5	12.93	2.62
C_2Cl_6	9.378	1.90

Table 8.

Results from the irradiation of methylene chloride

	In the presence of air		In vacuum	
Volume irradiated	435 mls		78.5 mls	
Dose Rate	8.41×10^{16} eV/cc/min		3.46×10^{16} eV/cc/min	
Irradiation time	110 hours		209 hours	
Product	Moles of product $\times 10^{3}$	G - value	Moles of product $\times 10^{4}$	G - value
HCl	24.77	5.32	33.18	5.06
$CHCl_3$	trace	< 0.1	trace	< 0.1
CH_3Cl	~ 6.9	~ 1.5	not determined	-
sym - $C_2H_4Cl_2$	0.9311	0.20	1.708	0.26
1, 1, 2 - $C_2H_3Cl_3$	2.328	0.50	5.257	0.80
sym - $C_2H_2Cl_4$	11.63	2.50	25.63	3.90

DISCUSSION

The products chlorine and hexachlorethane from irradiated carbon tetrachloride may be readily accommodated in a reaction scheme involving homolytic splitting of the carbon-chlorine bond as the primary stage, followed by dimerisation of the free radicals formed, to yield molecular chlorine and hexachlorethane.

$$CCl_4 \longrightarrow CCl_3^{\bullet} + Cl^{\bullet} \qquad \text{----------(1)}$$

$$2CCl_3^{\bullet} \longrightarrow C_2Cl_6 \qquad \text{----------(2)}$$

$$2Cl^{\bullet} \longrightarrow Cl_2 \qquad \text{----------(3)}$$

In the last irradiated solution examined, a trace of tetrachlorethylene was detected and although this observation must be treated with some reservation, since repetition has not so far been attempted, the possible production of tetrachlorethylene may arise from the reaction:

$$2CCl_3^{\bullet} \longrightarrow C_2Cl_4 + Cl_2$$

This may occurr with particularly reactive radicals; a similar type of elimination reaction is postulated tc account for certain products obtained from the radiolysis of chloroform. This will be discussed later.

The production of small amounts of hydro g en chloride and phosgene, even when the carbon tetrachloride was irradiated in the absence of air is believed to be due to primary radicals reacting with traces of water on the surface of the glass.

$$CCl_3^{\bullet} + HOH \longrightarrow CCl_3OH + H^{\bullet}$$

$$CCl_3OH \longrightarrow COCl_2 + HCl$$

$$H^{\bullet} + CCl_4 \longrightarrow CCl_3^{\bullet} + HCl$$

The effect of oxygen is shown by the lower G-values for hexachlorethane from the solutions irradiated in the presence of dissolved air. It is suggested that the initial concentration of dissolved oxygen in the stoppered irradiation vessel acts as an inhibitor to the normal reactions (2) and (3), and once this oxygen has been used, the irradiation mechanism proceeds normally. This suggestion might be confirmed by irradiating carbon tetrachloride solutions containing dissolved air for a number of low total doses, and showing that the G-value increased as the total dose increased up to a certain value.

In the irradiation of carbon tetrachloride in the absence of air, the measured yields of chlorine and hexachlorethane agree very closely for the overall reaction:

$$2CCl_4 \longrightarrow Cl_2 + C_2Cl_6$$

A mean G-value of 0.87 ± 0.04 is obtained for either product from this overall reaction. Prevot-Bernas et al.[43] investigated the radiolysis of carbon tetrachloride, and they observed a G-value of 70 for radical production in the presence of the radical scavenger D.P.P.H. They regarded this value with doubt however and recently Chapiro[70] has placed this value at 20.

Wild[71] has observed that D.P.P.H. is itself affected by gamma-radiation but, nevertheless, a detailed mechanism for reaction (1) must include reversal steps of very considerable importance to account for the low G-value of 0.87. Consider the reactions:

$$CCl_3^{\bullet} + Cl^{\bullet} \longrightarrow CCl_4 \qquad \text{-----(4)}$$

$$CCl_3^{\bullet} + Cl_2 \longrightarrow CCl_4 + Cl^{\bullet} \qquad \text{-----(5)}$$

$$Cl^{\bullet} + C_2Cl_6 \longrightarrow CCl_4 + CCl_3^{\bullet} \qquad \text{-----(6)}$$

Reactions (4) and (5) are known to be exothermic to the extent of 70 and 10 kilo calories per mole respectively[72]; reaction (6) is likely

to be endothermic. Processes (4) and (5) are believed to represent the two operative reversal steps and the latter has been examined recently by Schulte[67]. who irradiated carbon tetrachloride containing dissolved chlorine gas with gamma-rays. His findings have already been mentioned (page 30). It is interesting to note, that at comparable dose rates, he has obtained a G-value of 0.80 ± 0.06 for chlorine gas or hexachlorethane formation. He interprets his G = 3.25 for chlorine exchange as a measure of the radical yield of the reaction.

The G-values for the products from the radiolysis of chloroform, with the exception of G(HCl) are greater for chloroform irradiated in vacuum. Schulte et al.[66] have shown that the γ- ray induced decomposition of chloroform in the presence of oxygen proceeds by a chain mechanism. They observed that the types and quantitites of decomposition products existing at any one time depended on the oxygen concentration and the length of the irradiation. Possibly therefore the increased G(HCl) arises from a short chain reaction occurring while there is a concentration of oxygen available. When this is exhausted, the normal reaction about to be discussed will come into operation accounting for the products.

As in the case of carbon tetrachloride, the primary stage in the reaction mechanism for the decomposition of chloroform is taken to be the homolytic splitting of the carbon-chlorine bond. This may be followed by hydrogen atom abstraction by each of the free radicals formed, and thereafter the predominant process is believed to be the dimerisation of the free radicals. The mechanism proposed is the following:

$$CHCl_3 \longrightarrow CHCl_2^{\bullet} + Cl^{\bullet} \qquad \text{-----(1)}$$

$$CHCl_3 + Cl^{\bullet} \longrightarrow CCl_3^{\bullet} + HCl \qquad \text{-----(2)}$$

$$CHCl_3 + CHCl_2^{\bullet} \longrightarrow CCl_3^{\bullet} + CH_2Cl_2 \qquad \text{-----(3)}$$

$$2CCl_3^{\bullet} \longrightarrow C_2Cl_6 \qquad \text{-----(4)}$$

$$2CHCl_2^{\bullet} \longrightarrow C_2H_2Cl_4 \qquad \text{-----(5)}$$

$$CHCl_2^{\bullet} + CCl_3^{\bullet} \longrightarrow C_2HCl_5 \qquad \text{-----(6)}$$

$$CCl_3^{\bullet} + Cl^{\bullet} \longrightarrow CCl_4 \qquad \text{-----(7)}$$

$$CCl_3^{\bullet} + CHCl_3 \longrightarrow CCl_4 + CHCl_2^{\bullet} \qquad \text{-----(8)}$$

A similar reaction mechanism was proposed by Semeluk and Bernstein[73] to account for the products from the thermal decomposition of gaseous chloroform at approximately 500°C.

The above mechanism explains the C_1 and C_2 saturates, but not the appearance of tetrachlorethylene or the C_3 and C_4 products. It must be admitted at this point that a reaction mechanism involving, as the primary stage, the homolytic splitting of the carbon-hydrogen bond, rather than the carbon-chlorine bond, as has been observed in the benzoyl peroxide induced decomposition of chloroform[74], would explain the C_1 and C_2 products. However, it fails completely to account for the yields of the different products whereas the other mechanism does give a reasonable agreement. For example the G-values for the formation of the trichloromethyl radicals, according

to the proposed reaction scheme, may be written as:

$$G(CCl_3^{\bullet}) = G(HCl) + G(CH_2Cl_2)$$

$$= 4.28 + 1.35$$

$$= \underline{5.63}$$

Also the G-value for the removal of the trichlormethyl radicals may be written as:

$$G(-CCl_3^{\bullet}) = 2G(C_2Cl_6) + G(CCl_4) + G(C_2H\ Cl_5)$$

$$= 4.76 + 0.05 + 0.97$$

$$= \underline{5.78}$$

The agreement is reasonable.

Cherniak et al.[75] irradiated chloroform in the presence of a ferric salt, and they observed that the ferric reduction yield G (- Fe (111)) was 4.7. They were uncertain whether G could be identified with the radical yield G (R). However Prevôt-Bérnas et al.[43] using the D.P.P.H. radical scavenger technique obtained a value for G (R) of 65. It is interesting to note that these same workers observed that D.P.P.H. solutions gave identical results in the presence of air and in vacuum.

In order to account for the appearance of tetrachlorethylene, it is suggested that when two radicals combine, then occasionally elimination reactions occur if sufficient energy is available e.g.

$$CCl_3^{\bullet} + CHCl_2^{\bullet} \longrightarrow CCl_2 = CCl_2 + HCl \quad \text{-----(9)}$$

$$CCl_3^{\bullet} + CCl_3^{\bullet} \longrightarrow CCl_2 = CCl_2 + Cl_2 \quad \text{-----(10)}$$

$$CHCl_2^{\bullet} + CHCl_2^{\bullet} \longrightarrow CHCl = CCl_2 + HCl \qquad \text{-----(11)}$$

Semeluk and Bernstein[73] observed that tetrachlorethylene and hydrogen chloride were the major products from the thermal decomposition of gaseous chloroform and they favour biradical formation to account for the formation of tetrachlorethylene viz.

$$CCl_3^{\bullet} \longrightarrow CCl_2^{\bullet\bullet} + Cl^{\bullet}$$

$$CHCl_3 + CCl_2^{\bullet\bullet} \longrightarrow C_2Cl_4 + HCl$$

Considering again reactions (9), (10) and (11), the survival of tetrachlorethylene may be attributed to its lesser reactivity to addition reactions, whereas trichlorethylene might be expected to add radicals rapidly and be converted to C_3 or C_4 products e.g.

$$CHCl = CCl_2 + Cl^{\bullet} \longrightarrow CHCl_2CCl_2^{\bullet} \qquad \text{-----(12)}$$

$$CHCl_2CCl_2^{\bullet} + CCl_3^{\bullet} \longrightarrow CHCl_2CCl_2CCl_3 \qquad \text{-----(13)}$$

In order to evaluate the importance of a process such as (12) dilute solutions of trichlorethylene in chloroform are at present being irradiated in this department.

Interesting results have already been obtained from the irradiation of a 10% solution of tetrachlorethylene in chloroform (see table 5). The G-value for hydrogen chloride is reduced and there is a three fold increase in the G-value for pentachlorethane, compared with the corresponding value for irradiated pure chloroform.

In addition comparison of the two G.P.C. chromatograms showed that one of the peaks representing a C_3 or C_4 product was increased in area by a factor of approximately 1.5. Reactions similar to (12) and (13), but involving tetrachlorethylene molecules would appear to have occurred. If a reaction similar to (12) assumed importance then this would account for the lower G-value for hydrogen chloride because fewer chlorine atoms would then be available for reaction (2) responsible for hydrogen chloride formation.

Also it is suggested that the increased penta chlorethane yield may arise from the addition of hydrogen chloride across the double bond of tetrachlorethylene.

$$CCl_2 = CCl_2 + HCl \longrightarrow CHCl_2CCl_3$$

This reaction would also contribute to the low observed G-value for hydrogen chloride production.

The irradiation of methylene chloride has been studied less thoroughly than chloroform of carbon tetrachloride. Once again the observed G-values, with the exception of G-value for hydrogen chloride, are lower when the irradiation is carried out in the presence of dissolved air.

It is believed that a mechanism analogous to that discussed for chloroform applies viz.

$$CH_2Cl_2 \longrightarrow CH_2Cl^{\bullet} + Cl^{\bullet}$$

$$CH_2Cl_2 + Cl^{\bullet} \longrightarrow CHCl_2^{\bullet} + HCl$$

$$CH_2Cl_2 + CH_2Cl^{\bullet} \longrightarrow CHCl_2^{\bullet} + CH_3Cl$$

$$2CHCl_2^{\bullet} \longrightarrow C_2H_2Cl_4$$

$$CHCl_2^{\bullet} + CH_2Cl^{\bullet} \longrightarrow C_2H_3Cl_3$$

$$CHCl_2^{\bullet} + Cl^{\bullet} \longrightarrow CHCl_3$$

The C_2 unsaturates arising from reactions analogous to reactions (9), (10) and (11) for the chloroform reaction mechanism will be:

(i) trichlorethylene (ii) vinyl chloride

(iii) vinylidene chloride (iv) 1, 2-dichlorethylene

None of these unsaturates have been detected and this is not surprising, when it is considered that other workers in this department[47], have shown that the mono, di and tri-chlorinated ethylenes are readily polymerised by gamma radiation. It is of interest to note that in a preliminary experiment on irradiated methylene chloride, vigorous decomposition and charring of some solid material occurred where there was local overheating during the concentration of the main solution. The same workers have shown that some of the polymers from irradiated chlorinated ethylenes decompose and char on overheating.

Since there are four possible unsaturates from methylene chloride compared with the two from chloroform, it is not surprising that four peaks were observed on the G.P.C. chromatogram representing four C_3 or C_4 products compared with the three observed for irradiated chloroform.

The very low G-values for chlorine or hexachlorethane from carbon tetrachloride relative to the G-value for hydrogen chloride from chloroform and methylene chloride indicates considerable reversal reactions. Further evidence, for the occurrence of reversal reactions in the irradiation of pure carbon tetrachloride, was obtained by irradiating a 50% solution of

chloroform in carbon tetrachloride, when it was observed that the G-values for hydrogen chloride and hexachlorethane respectively, were greater than the corresponding G-values observed from pure chloroform. (see tables 5 and 6).

The extent of the reversal reactions was examined further by irradiating a 10% solution of chloroform in carbon tetrachloride. It was believed that a high yield of hexachlorethane, matched by a comparable hydrogen chloride yield, would result from the following processes:

$$CCl_4 \longrightarrow CCl_3^{\bullet} + Cl^{\bullet}$$

$$Cl^{\bullet} + CHCl_3 \longrightarrow CCl_3^{\bullet} + HCl$$

$$2CCl_3^{\bullet} \longrightarrow C_2Cl_6$$

It was thought that this would give a reliable estimate of the extent of the primary decomposition. However, although a high yield of hexachlorethane was obtained $G(C_2Cl_6) = 3.20$, the yield of hydrogen chloride was higher at $G(HCl) = 4.10$, and therefore the decomposition of chloroform itself must be taken into account. In fact a trace of pentachlorethane was detected in the reaction mixture. More informative results would probably be obtained by irradiating very dilute solutions of chloroform in carbon tetrachloride (e.g. 1%) when there would be more justification for ignoring the primary decomposition of the chloroform.

Finally it was observed on the G.P.C. chromatogram from the irradiated 50% chloroform - carbon tetrachloride solution, that the yield of one of the C_3 or C_4 products from irradiated pure chloroform was

apparently increased by the addition of carbon tetrachloride as a source of trichlormethyl radicals. This together with the observations from irradiated 10% tetrachlorethylene in chloroform (page 53) support the original suggestion that the C_3 and C_4 products arise by addition of C_1 radicals at the double bond of the unsaturates.

Probably the easiest way to identify these compounds would be to synthesise some chlorinated C_3 and C_4 products and compare their retention times on a G.P.C. chromatogram with those of the unknown irradiation products.

SECTION II

The irradiation of the chlorinated ethylenes: 1, 1 - dichlorethylene and tetrachlorethylene, and the irradiation of the allyl halides: allyl chloride, allyl bromide and allyl iodide.

INTRODUCTION

The ease of polymerisation of 1, 1 - dichlorethylene (vinylidene chloride) was noted by Bauman[76] in 1872, who observed the formation of a white solid polymer from vinylidene chloride exposed to sunlight. Since then other workers have observed that vinylidene chloride polymerises quickly in the light, or slowly when kept in the dark.[77] Reinhardt[78] has reviewed this field and describes the ease with which vinylidene chloride is polymerised by refluxing in the presence of organic and inorganic peroxides, organic carbonyl compounds, organometallic compounds, and inorganic salts and acids. For example, refluxing at 45°C in the presence of 0.5 mole per cent of benzoyl peroxide results in 90% conversion after 40 hours. Photopolymerisation has also been successful, with and without auxiliary chemical catalysts, and at temperatures as low as -35°C.

Carefully purified vinylidene chloride free from oxygen polymerises very slowly. As ordinarily prepared however, vinylidene chloride polymerises readily, due to the presence of oxygen which reacts to form acid chlorides and peroxides which catalyse the polymerisation[79].

The early workers such as Feist[77], Staudinger[80], and Brunner[81] observed that poly-vinylidene chloride possessed three outstanding characteristics - crystallinity as determined by X-ray powder photographs, insolubility in the common organic solvents, and resistance to acid and alkali, although they noted that discolouration was caused by concentrated sulphuric acid or concentrated ammonia. Staudinger[80] assigned to poly-vinylidene chloride the "head to tail" configuration

$$\text{------} - CH_2 - CCl_2 - CH_2 - CCl_2 - \text{------}$$

and attributed its crystallinity to its regular molecular structure.

Commercially, vinylidene chloride is co-polymerised with 10% vinyl chloride and sold under the name of "Saran", as a white crystalline polymer which finds many industrial uses[82].

1, 2-dichlorethylene and also trichlorethylene have proved more difficult to polymerise by the conventional methods, with low yields of mainly low molecular weight oil polymers[83]. Stafford and Taylor[47], in this department, using gamma-rays, obtained liquid polymer from cis and trans dichlorethylene, and in addition, a non-crystalline solid polymer from trans-dichlorethylene. This gamma-ray induced polymerisation process has now been patented.

The polymerisation of trichlorethylene by gamma-rays investigated by the same workers[47], presented no novel features except that explosive gases were produced together with the low yield of liquid polymer. They suggest that the gases might be chloracetylenes produced by decomposition of vinyl radicals. Low yields of liquid polymer have also been observed from trichlorethylene by other workers using pressure vessels and temperatures between 150 and 200°C.[84]

Previous attemps to polymerise tetrachlorethylene have been largely unsuccessful, although in a recent paper, Gonikberg and Zhulin[85] claim to have obtained a 56% yield of hexachlorethylene and hexachloro-1, 3-butadiene from tetrachlorethane in a steel bomb at 300°C for 56 hours.

One of the earliest observations of polymeric material from the allyl halides is attributed to Staudinger and Fleitmann[86], in 1930, who illuminated allyl chloride with ultra-violet light over a period of several weeks and noted the formation of very viscous liquid polymers.

By a study of the reduced product from the photopolymerisation of allyl chloride, Staudinger and Fleitmann[86] concluded that its structure was

essentially as shown below:

$$n\ CH_2 = CH - CH_2Cl \longrightarrow \left[- CH_2 - \underset{\displaystyle CH_2Cl}{\underset{|}{CH}} - \right]_n$$

The low volatility and the fire-resistant qualities of these polymers, suggested such applications as plasticizers and wood impregnators, and many processes were patented for their formation. For example, Bauer and Gotz[87], by heating allyl chloride with benzoyl peroxide at a high temperature in a pressure vessel, have obtained a viscous liquid polymer with an average of six allyl chloride units per molecule. A polymer of about four units per molecule was made by treating allyl chloride with boron trifluoride in the presence of Raney nickel at low temperatures.[88]

Similar polymer material has only been obtained in very small yields from allyl bromide and allyl iodide.[86]

The gamma-ray induced polymerisation of some chlorinated ethylenes and allyl halides will now be described.

EXPERIMENTAL

The irradiation of tetrachlorethylene in the presence of air.

Extra pure tetrachlorethylene from E. Merck A.G. Darmstadt was well shaken several times with dilute acid until no yellow colour was evident in the acid layer. This procedure was adopted to remove the basic compound present as a stabiliser. The organic layer was then washed several times with water and dried with phosphorus pentoxide. It was distilled immediately before use under reduced pressure using a short Vigreux fractionating column: (b.p. 52°C/60 m.m.). The first and last 10% portions of the distillate were rejected.

N_{20}^{D} = 1.5054 (Lit. N_{20}^{D} = 1.5018).

A G.P.C. analysis gave no indication of any impurities present.

Technical grade tetrachlorethylene from Hopkin and Williams was subjected to the same purification procedure and the distillation was carried out using a more efficient fractionating column. However the refractive index of this compound was still high viz. N_{20}^{D} = 1.5056.

393 mls of purified tetrachlorethylene were irradiated in a stoppered annular glass vessel at a dose rate of 6.38×10^{16} eV/cc/min for 232 hours.

Phosgene (by smell) and hydrogen chloride (ammonia test) were detected when the stoppers were removed; the irradiated solution was pale yellow in colour. Unchanged tetrachlorethylene was removed by distillation under reduced pressure and during the distillation a white crystalline sublimate collected in the water condenser. The residual product was 12 gms of a red viscous oil which give G = 9 referring to the total polymer yield expressed as monomer units.

About 300 mg of sublimate were removed from the water condenser with 40/60 petrol ether then purified by sublimation. It was shown to be hexachlorethane by the methods described previously (see page 33).

The 12 gms of oil product were separated into four fractions by a vacuum distillation using a small fractionating column. The oil bath temperature (O.B.T.) for each fraction collected is given, rather than the temperature observed at the top of the Vigreux column, for this was found to fluctuate due to insufficient vapour being present to give a true boiling point reading. The quantities of fractions listed are approximate.

Fraction I	100 mgs of white crystalline solid	OBT 40-60°C/10^{-2}mm.
Fraction II	2 gms of colourless oil	OBT 60-80°C/10^{-2}mm.
Fraction III	400 mgs of white crystalline sublimate	OBT 70-100°C/10^{-2}mm.
Fraction IV	8 gms of red viscous oil	OBT 120-180°C/10^{-2}mm.

Fraction I was identified as a further quantity of hexachlorethane.

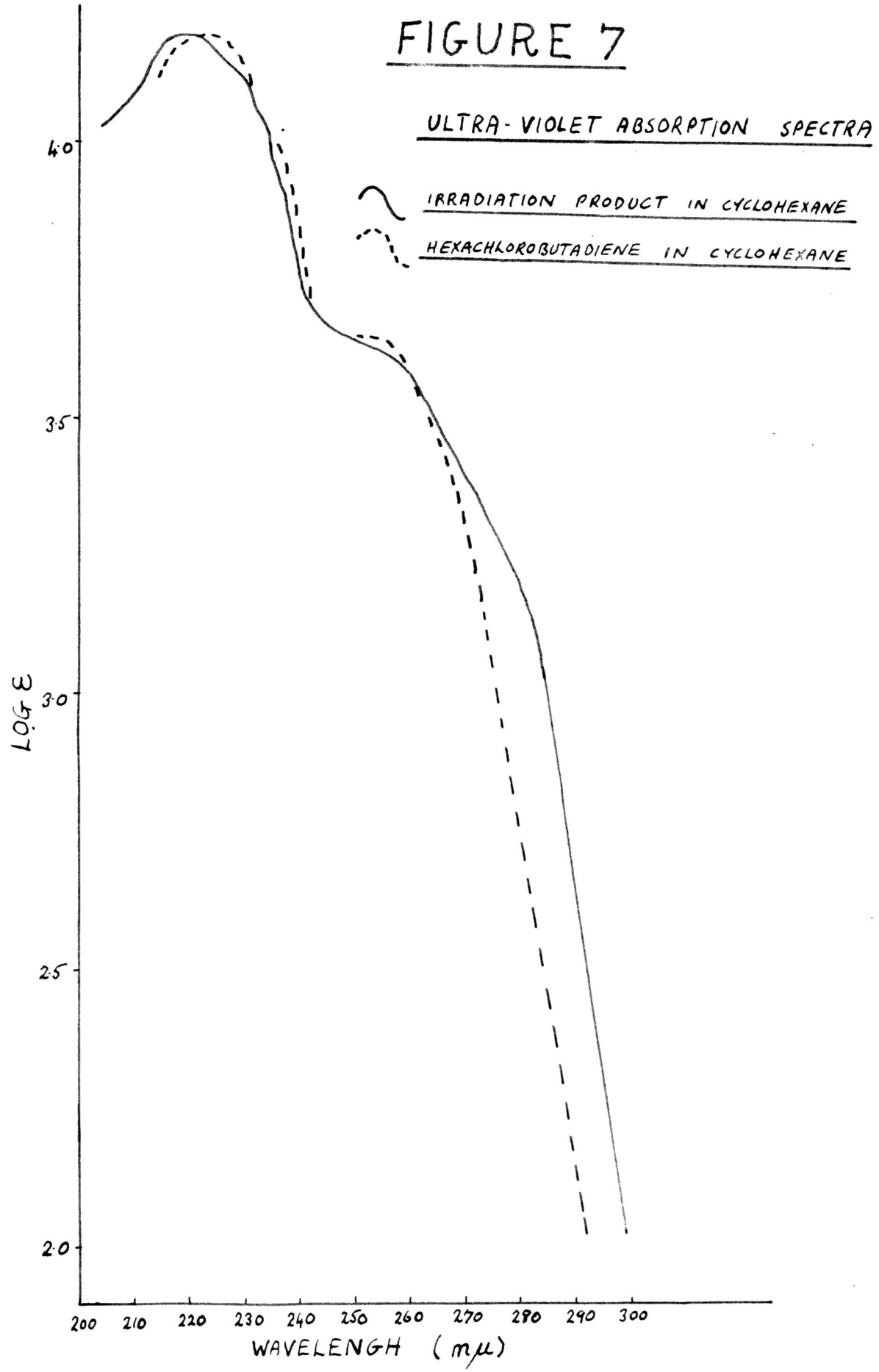
Fractions II and IV were redistilled and fraction III was re-crystallised from absolute ethanol. An infra-red report was received from Harwell on each of the fractions.

A chemical analysis of the first liquid fraction suggested an empirical formula C_4Cl_6.

Analysis Found		Analysis calculated for C_4Cl_6	
C =	18.1%	C =	18.4%
H =	0.5%	Cl =	81.6%
Cl =	81.3%		
Total =	99.9		

The compound was stable to acid and alkali, and had a strong absorption in the ultra violet with a maximum at 220.5 m μ corresponding to ε = 15,780. The infra red spectrum revealed two intense absorption bands in the C = C stretching region and the spectrum closely resembles the spectrum of hexachloro - 1, 3 - butadiene given by Szasz and Sheppard.[89] The irradiation

FIGURE 7


ULTRA-VIOLET ABSORPTION SPECTRA
IRRADIATION PRODUCT IN CYCLOHEXANE
HEXACHLOROBUTADIENE IN CYCLOHEXANE
LOG ε
4·0
3·5
3·0
2·5
2·0
200
210
220
230
240
250
260
270
280
290
300
WAVELENGH (mμ)

product would therefore appear to be hexachloro -1, 3-butadiene and this has been confirmed by the following physical measurements:

$N_{20}^{D} = 1.5549$ (Lit. $N_{20}^{D} = 1.5542$)

$d^{20} = 1.675$ (Lit. $d_{4}^{20} = 1.6820$)

Molecular weight = 260 and 254 (M. Wt. = 261)

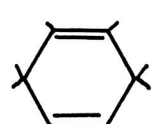
The molecular weights were determined by depression of the freezing point of pure benzene.

Final confirmation was obtained by a comparison of the ultra-violet spectra of the irradiation product dissolved in spectroscopic ethanol, with that of pure hexachloro-1, 3-butadiene disolved in the same solvent (see figure 7).

The solid obtained as Fraction III was contaminated with an oil fraction and it was pressed on filter paper several times then recrystallised from absolute ethanol. Prisms were obtained with a strong camphor-like odour. mp = 162-163°C, accompanied by slight sublimation from 130°C onwards. The density of this material was obtained by floating one of the crystals in a prepared methyl iodide-ethanol solution, the density of which could be varied by the addition of ethanol or methyl iodide. $d^{20} = 2.024$.

X-ray powder photographs of authentic hexachlorethane and hexachlorobenzene were compared with that of the irradiation product and the three were unmistakably different. Data obtained from the X-ray powder photograph, in conjunction with the density value of 2.024, placed the molecular weight of this material in the region of 350.

A chemical analysis gave the material a formula C_6Cl_8, which suggested an octachlorohexatriene or an octachloro-cyclohexadiene structure, i.e.

C = C - C = C - C = C or 

Analysis found		Analysis calculated for C_6Cl_8	
C	= 20.1%	C	= 20.2%
H	= 0.2%	Cl	= 79.8%
Cl	= 80.2%		
Total	100.5%		

The material dissolved in cyclohexane had a strong absorption in the ultra-violet and there was a maximum at 225 m μ (e = 16,531). An unsaturated structure was also suggested by the infra-red report, which revealed the presence of two intense absorption bands in the C = C stretching region of the spectrum at 1641 cms^{-1} and 1607 cms^{-1}. The report suggests that since these same C = C absorption bands for the compound hexachlorobutadiene, recorded by Szasz and Sheppard[89], lie at a much lower frequency than those observed for the solid irradiation product, it would seem reasonable to interpret this large frequency shift, on the basis that the solid has a ring structure, in which case the two observed bands could be assigned to some form of ring stretching vibration.

Accordingly the solid is believed to be octachloro-cyclohexadiene. Its constants were compared with these given in the literature for octachloro - 1, 4 - cydohexadiene:

d^{20} = 2.024 (Lit. d^{20}_4 = 2.0621)

m.p. = 162-63°C (Lit. m.p. = 160°C)

Molecular weight = 350 (M.Wt. = 356)

However, by reason of the very strong absorption in the ultra-violet, the material has been assigned a conjugated 1, 3 - cyclohexadiene structure rather than that of the 1, 4 - diene.

A synthesis of octachloro - 1, 4 - cyclo hexadiene, following the method described by Barral[90], was unsuccessful, principally because insufficient starting material was available. 5.5 gms of tetrahydroquinone were used and the small yield of white crystalline product was shown by G.P.C. analysis to contain 60% of hexachlorobenzene. Barral recrystallised his product several times, and after a final slow crystallisation procedure, he separated mechanically, two types of crystals, viz. needles of hexachlorobenzene, and prisms of octachloro-cyclo hexadiene. However he used 30 gms of tetrahydroquinone and obtained a small yield of pure product.

The 8 gms of red viscous oil obtained as the final product fraction from irradiated tetrachlorethylene was redistilled in vacuum using a molecular cup still apparatus. Two fractions were obtained:

Fraction I 3.0 gms of red viscous oil OBT 100 - 120°C/10^{-4} mm.

Fraction II 5.0 gms of red very viscous oil OBT 140 - 180°C/10^{-4} mm.

Fraction II on cooling formed a red 'glassy' solid and no further work was done on this product.

A chemical analysis of fraction I suggested the empirical formula C_4Cl_8; molecular weight determinations by depression of the freezing point of pure benzene gave the values 338 and 332.

Analysis found		Analysis calculated for C_4Cl_8
C = 14.3%		C = 14.5%
H = 0.5%		Cl = 85.5%
Cl = 85.3%		Molecular weight = 332
Total = 100.1		

The compound absorbs in the ultra violet to a much less degree than the other tetrachlorethylene irradiation products and there is a maximum at

213 m μ (ϵ = 1845). In the infra-red spectrum, bands of weak intensity occur in the C = C stretching region. According to Bellamy[91], it can be predicted from theoretical considerations that no C = C stretching vibration will appear in the infra-red from compounds with a trans double bond at a centre of symmetry, and in many cases, the absorption from the cis double bond is extremely weak. Therefore the compound is believed to be an octachlorobutene-1 rather than the butene-2. An ozonisation, in an attempt to confirm the butene-1 structure, was unsuccessful. The compound would appear to be quite resistant to ozone, for only starting material was obtained at the end of the experiment.

The refractive index found was N^{D}_{20} = 1.5844 and from the literature a definite mixture of the two isomers has been found to have a value N^{D}_{20} = 1.5789.

To summarize - from the irradiation of tetrachlorethylene the following products have been isolated:

(1) Hexachloro -1, 3- butadiene.

(2) Octachloro-cyclo hexadiene believed to be the 1, 3- diene.

(3) Octachlorobutene believed to be the 1- butene.

In addition red semi-solid polymer oil was obtained as the major product. The calculated G-value for the conversion of tetrachlorethylene molecules into product is 9.

The irradiation of tetrachlorethylene in the absence of air.

A tube of purified tetrachlorethylene was degassed and sealed off in the absence of air as described previously for the halogenated methanes.

80 mls were irradiated for 143 hours at a dose rate of 3.46×10^{16} eV/cc/min.

No phosgene or hydrogen chloride were detected at the end of the irradiation period.

The irradiated solution was distilled down to a volume of approximately 10 mls and the concentration of hexachlorethane and hexachloro -1, 3- butadiene was determined by a G.P.C. analysis. The hexachlorethane result probably represents a lower limit, rather than an absolute value, for it was shown experimentally that hexachlorethane readily co-distills with tetrachlorethylene. An accurate value for hexachlorethane can only come from a prolonged irradiation at a high dose rate, when it will not be necessary to concentrate the tetrachlorethylene solution for the detection of products. It has not yet been possible to analyse the other products from tetrachlorethylene by G.P.C. analysis. Results:

Product	Moles of Product	G - value
C_2Cl_6	3.172×10^{-3}	0.59
C_4Cl_6	6.227×10^{-3}	1.16

The irradiation of hexachloro -1, 3- butadiene

Hexachlorobutadiene from Light and Co. was purified by one distillation under reduced pressure using a Widmer fractionating column. The first and last 10% portions of the distillate were discarded b.p. 96°C/18 m.m.

$$N_{20}^{D} = 1.5560 \quad (\text{Lit. } N_{20}^{D} = 1.5542)$$

390 mls were irradiated in a stoppered annular glass vessel at a dose rate of 6.38×10^{16} eV/cc/min for 452 hours.

Phosgene and hydrogen chloride were detected. Unchanged hexachlorobutadiene was removed by distillation under reduced pressure leaving 12.5 gms of a red viscous oil. This was transferred to a small flask attached to a short Vigreux fractionating column and fractionally distilled under high vacuum conditions. Four fractions were collected.

Fraction I	:	Red brown viscous liquid	OBT 90-120°C/10^{-3} mm.
Fraction II	:	" " " "	OBT 120-150°C/10^{-3} mm.
Fraction III	:	" " " "	OBT 150-200°C/10^{-3} mm.
Fraction IV	:	" " " "	OBT 200-250°C/10^{-3} mm.

None of these fractions corresponded to any of the products from irradiated tetrachlorethylene; even after fraction I was carefully distilled into five fractions no correspondence could be obtained.

It would appear that hexachloro-1, 3-butadiene upon irradiation polymerises to give perhaps perchloro C_8 or C_{12} fractions but this requires further investigation.

The irradiation of an equimolar tetrachlorethylene - hexachlorobutadiene solution

390 mls of an equimolar solution were irradiated in a stoppered annular glass vessel for 360 hours at an unspecified dose rate.

The unchanged tetrachlorethylene and hexachlorobutadiene were removed by distillation under reduced pressure. During the distillation about 250 mgms of white crystalline sublimate collected in the water condenser. This was shown to be hexachlorethane by the methods previously described on page . The viscous product was 20 gms of a viscous red brown oil which was fractionally distilled, as described in previous experiments, into a number of fractions.

Fraction I	:	Yellow brown viscous oil	OBT 100-130°C/10^{-3} mm.
Fraction II	:	" " " "	OBT 130-150°C/10^{-3} mm.
Fraction III	:	Dark " " "	OBT 150-210°C/10^{-3} mm.

No solid material appeared in any of these fractions and they were not examined further.

The irradiation of 1, 1-dichlorethylene (vinylidene chloride)

Technical grade vinylidene chloride from I.C.I. was distilled immediately before use. b.p. 36-38°C.

5 litres of this liquid were irradiated in a stoppered annular glass vessel for approximately 1200 hours.

During the irradiation polymerisation occurred very rapidly and polymer entered the source tube, preventing the cobalt-60 source from being withdrawn into the concrete block. Consequently the vinylidene chloride received a very large dose before the difficulty was overcome. The entire solution polymerised to a white solid which was removed by breaking the flask. Much hydrogen chloride and phosgene were evident.

The solid was observed to be resistant to concentrated acid and alkali and was insoluble in all the common organic solvents. It was soluble in nitrobenzene, tetrachlorethane and pentachlorethane although no crystal formation was observed.

The solid was stable to heat to 145°C then it began to soften and at 175°C complete conversion to an oil had occurred. Resolidification occurred on cooling.

The irradiation of allyl chloride

B.D.H. allyl chloride was distilled immediately beforeuse using a Vigreux fractionating column. The first and last 10% fractions of the distillate were discarded. b.p. 43-44°C. N^{D}_{20} = 1.4160 (Lit. N^{D}_{20} = 1.4160).

15 cc. of allyl chloride were irradiated in a stoppered quick-fit test-tube attached to the side of the 140-Curie source for 200 hours at an unspecified dose rate.

Unchanged allyl chloride was removed by distillation and the

residual product was 2 gms of a viscous colourless oil. A distillation of this oil using a molecular still was attempted at OBT $250^{o}C/10^{-4}$ mm. without any success. The product did not distill, and even at $250^{o}C$ no decomposition was observed to occur.

Upon irradiation of 370 mls of allyl chloride in a stoppered annular glass vessel for 300 hours at an unspecified dose rate, 35 gms of viscous colourless oil were obtained as product. This, when molecularly distilled, gave one fraction. viz. 0.5 mls of colourless viscous liquid OBT $150^{o}C/10^{-4}$ mm.

A chemical analysis of the residual product gave the empirical formula C_3H_5Cl which is that of allyl chloride itself.

Analysis found	Analysis calculated for C_3H_5Cl
C = 46.8%	C = 47.1%
H = 6.7%	H = 6.5%
Cl = 46.6%	Cl = 46.4%
Total = 100.1	Molecular weight = 76.5

The molecular weight of the product was determined by depression of the freezing point of pure benzene as 394 and therefore it is suggested that the viscous oil is an allyl chloride polymer of average degree of polymerisation equal to 5.

Hydrogenation of this polymer oil with hydrogen using platinum oxide as a catalyst was unsuccessful; a slow Halogenolysis reaction being observed to occur. No reaction occurred with lithium aluminium hydride or ozone, and a Grignard reaction using dry ether and magnesium turnings was also unsuccessful. In each case unchanged starting material was obtained at the end of the reaction.

Irradiation of allyl bromide

Allyl bromide from B.D.H. was purified by one distillation under reduced pressure. b.p. 54°C/515 mm.

N_{20}^{D} = 1.4670 (Lit. N_{20}^{D} = 1.4654)

A quick-fit test tube containing 15 mls of colourless liquid was irradiated in a similar position to that occupied by the allyl chloride tube for the same length of time. viz. 200 hours.

The liquid was a yellow colour after irradiation. Upon removal of the unchanged allyl bromide by distillation under reduced pressure, approximately 0.5 gms of a viscous yellow oil were obtained as residual product. A molecular distillation of this product produced one fraction:

Approximately 0.2 gms of a colourless oil OBT 50-60°C/10^{-2} mm.

A very viscous yellow residue remained in the distillation flask and after several weeks this turned dark brown in colour.

The irradiation of allyl iodide

Allyl iodide from B.D.H. was distilled under reduced pressure. b.p. 56°C/180 mm.

15 mls of pale yellow liquid in a stoppered test-tube were given the same total dose of radiation as the other allyl halides.

The liquid was red in colour after irradiation. A thin film of dark tarry residue was left in the distillation flask after removal of unchanged allyl iodide.

No further examination was made of this system.

The irradiations of the allyl halides described were carried out for the purpose of comparing polymer formation from each of them. Recently, other

workers in this department have irradiated allyl fluoride[48], and have studied more carefully the irradiation of allyl bromide[47] by the use of G.P.C., in an attempt to determine intermediate products. Their results will be discussed later for comparison purposes.

DISCUSSION

It is suggested that the mechanism of the interaction of gamma radiation with chlorinated unsaturated compounds involves an initiation step similar to that already postulated for the decomposition of chloroform and carbon tetrachloride viz. homolytic splitting of the carbon-chlorine bond. However, in the case of the unsaturates, the double bond will more readily facilitate the occurrence of a chain reaction, and the chlorine atom formed by the initiation step, will attack further unsaturated molecules to promote chain formation. At any time these chains may terminate by a step involving any two free radicals. The following mechanism is proposed for tetrachlorethylene:

Initiation

$$CCl_2 = CCl_2 \longrightarrow CCl_2 = \dot{C}Cl + \dot{C}l \qquad \text{-----(1)}$$

Propagation

$$CCl_2 = CCl_2 + Cl^{\bullet} \longrightarrow {}^{\bullet}CCl_2 - CCl_3 \qquad \text{-----(2)}$$

$$CCl_2 = CCl_2 + {}^{\bullet}CCl_2 - CCl_3 \longrightarrow {}^{\bullet}CCl_2 - CCl_2 - CCl_2 - CCl_3 \qquad \text{-(3)}$$

$$CCl_2 = CCl_2 + {}^{\bullet}CCl_2 - (CCl_2)_N - CCl_3 \longrightarrow {}^{\bullet}CCl_2 - (CCl_2)_{N+2} - CCl_3 \qquad \text{-(4)}$$

Termination

$$CCl_2 = CCl^{\bullet} + {}^{\bullet}CCl_2 - CCl_3 \longrightarrow CCl_2 = CCl - CCl_2 - CCl_3 \qquad \text{--(5)}$$

$$2\ CCl_2 = \dot{C}Cl \longrightarrow CCl_2 = CCl - CCl = CCl_2 \qquad \text{--(6)}$$

$$CCl_2 = CCl_2 + {}^{\bullet}CCl_2 - CCl_3 \longrightarrow CCl_2 = \dot{C}Cl + CCl_3 - CCl_3 \qquad \text{--(7)}$$

$${}^{\bullet}CCl_2 - CCl_3 + Cl^{\bullet} \longrightarrow CCl_3 - CCl_3 \qquad \text{------(8)}$$

Such a reaction mechanism accounts for the observed reaction products from tetrachlorethylene except the cyclic compound which will be discussed later.

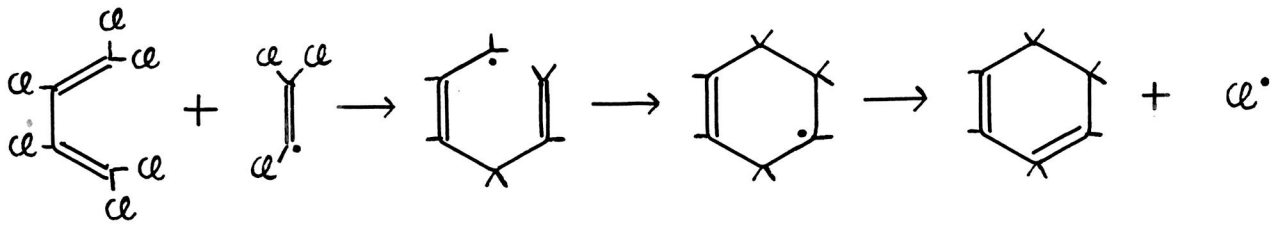
According to the proposed scheme, much more hexachlorethane should

be formed than is actually observed, but experience has shown that this compound is readily lost by co-distillation with unchanged tetrachlorethylene. A suggested technique for overcoming this difficulty in future experiments has already been mentioned in the experimental section (page 68).

Reaction (5) accounts for the octachlorobutene and reaction (6) for the hexachlorobutadiene. It is of interest to note that Stafford and Taylor[47] did not observe the formation of the appropriate diene from the radiation induced polymerisations of 1, 2-dichlorethylene and trichlorethylene. However they obtained much more higher molecular weight polymer, especially from the 1, 2-dichlorethylene. Therefore it is suggested that the formation of the diene can be regarded as a measure of the reactivity of the parent diene radical. The more reactive diene radicals from 1,2-dichlorethylene and trichlorethylene will react to yield more higher molecular weight product, while the less reactive (from the tetrachlorethylene molecule) will generally dimerise.

The major factor contributing to the small amount of polymerisation which occurs (G = 9) compared with the polymer formation from 1, 2-dichlorethylene (G (cis) = 142, G (trans) = 224) and trichlorethylene (G = 30) is believed to be the lack of reactivity of the symmetrical tetrachlorethylene molecule. This lack of reactivity of symmetrical perchloro compounds is well-known, and is manifested by the inability of hexachlorobutadiene to undergo the normal Diels Alder condensation reaction with maleic anhydride. Also hexachlorobutadiene ($G \sim 4$) was shown to be even more resistant to gamma-induced polymerisation than tetrachlorethylene.

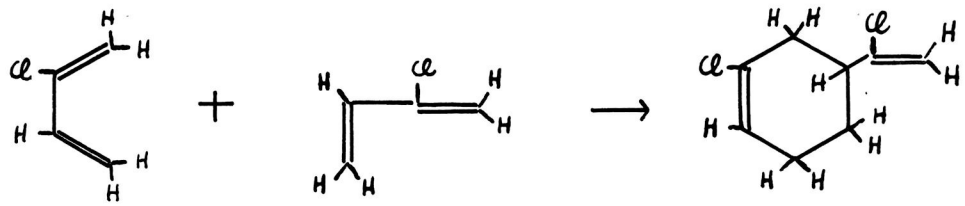
The following reaction scheme involving hexachlorobutadiene molecules was considered for the formation of the cyclic compound:



However no analogous products have been obtained from irradiation of the other chlorinated ethylenes, and it is difficult to explain why cyclisation should occur in the tetrachlorethylene polymerisation, when a less degree of steric hindrance in the other chlorinated ethylenes should favour cyclisation more readily.

Also according to this reaction scheme, the irradiation of a solution of hexachlorobutadiene in tetrachlorethylene would be expected to yield a greater quantity of cyclic product. In fact no cyclic material was observed from this experiment, although it is quite possible that any octachloro-cyclohexadiene formed during the irradiation, might have been lost by co-distillation during the removal of the unchanged hexachlorobutadiene and tetrachlorethylene by distillation.

It is worth noting that Brown et al.[92] have observed that chloroprene (2-chloro-1, 3-butadiene) dimerised on standing or heating in the presence of polymerisation inhibitors, yielding a mixture, from which a 6-membered cyclic dimer, and an 8-membered cyclic dimer were isolated. Under similar conditions, Foster and Schreiber[93] have isolated an 8-membered cyclic dimer from 2, 3-dichloro-1, 3-butadiene. Cope and Schmitz[94] have suggested that the vinyl cyclohexene from chloroprene could be explained by dimerisation by a normal Diels Alder addition reaction viz.



This is similar to the scheme considered for the formation of the 6-membered cyclic compound from tetrachlorethylene.

Very little can be said concerning the vinylidene chloride polymerisation. The G-value is of the order of thousands and the polymer obtained has all the properties common to the polymer obtained by the conventional means, although the softening point of the radiation polymer (145°C) is 40°C lower than that reported for the other polymer.

At the outset of the work there was little information available regarding the mechanism of the interaction of gamma radiation with unsaturated compounds, and therefore the initial experiments were designed to show whether gamma radiation caused bond-splitting or bond excitation. It might be expected that during the irradiation of 1, 2-dichlorethylene, where cis-trans isomerism occurs, there is the possibility that an excited molecule might revert to an unexcited form to some extent with change of configuration. However, Stafford and Taylor[47] observed neglible isomerisation upon irradiation of either pure isomer.

The bond excitation process would yield products on the whole which arise simply by union of two or more molecules without loss of any fragment .

Many of the major products isolated do, in fact, have an empirical monomer formula, but others give evidence of loss of chlorine atoms, which is in agreement with bond-splitting. In the latter process, the strength of the bonds would play some part in dictating the course of the reaction, and since it was known that the carbon-halogen link in allyl compounds is weaker than in vinyl compounds[95], the allyl halides were studied. If the reaction goes through an excited molecule, then it should be relatively independent of the halogen atom present. In fact a distinct difference was observed between the chloro compound on the one hand and the bromo and iodo compound on the other. While polymer was formed quite readily from allyl chloride, its formation from allyl bromide ana allyl iodide was very slight. This would suggest that there is a dependence on the carbon-halogen link. But the yields of product were greatest in the case of the one with the strongest bond. In this connection, Ehrlich and Stafford[48] studied the irradiation of allyl fluoride. They observed only a small yield of polymer.

Petry and Schuler[96] have observed that the predominant effect of radiolysis of liquid alkyl iodides is rupture of the carbon-iodine bond. Also Gevantmann and Williams[97] in similar studies noted that there was preferential fission of the weak carbon-iodine bond, for with labelled iodine present, the principal reaction was exchange.

The empirical monomer formula of the allyl chloride polymer is not in disagreement with an excited molecule mechanism and the yield of polymer is sufficiently high to suggest a reasonable polymerisation chain. On the other hand the failure of the other allyl halides to polymerise, is best accounted for by an initial carbon-halogen bond cleavage, in which case it can be proposed that the chain carriers are dissipated by alternative reactions involving

the halogen atoms.

In this respect, iodine was observed from the irradiation of allyl iodide, and it is worth noting that many workers, for example McCauley and Schuler[25], have made use of added iodine as an efficient radical scavenger in hydrocarbon radiolysis. The allyl iodide system requires to be re-examined with more attention paid to lower boiling products, which in previous experiments would be lost during the removal of unchanged allyl iodide by distillation under reduced pressure.

Recently Ehrlich and Stafford[48] restudied the irradiation of allyl bromide and noted the formation of products which can only be explained in terms of an initial carbon-bromine bond split. Although they did not detect free bromine molecules, they identified the product, 1, 2, 3-tribromopropane, which is best explained by the addition of a molecule of bromine across the double bond of an allyl bromide molecule.

S E C T I O N III

The irradiation of benzene, toluene and carbon tetrachloride solutions of these compounds.

INTRODUCTION

Although earlier observations were reported on the nature of the products from irradiated aqueous solutions of aromatic compounds,[8,9] work on the radiolysis of the pure aromatic compounds appears to have been limited to the last decade.

The yields of hydrogen, methane, and other gases, in addition to a small amount of polymer, when benzene and toluene were exposed to X-rays, were measured by Burton[98], in 1947, and a year later, Stein and Weiss[7] used X-rays to investigate the radiolysis of dilute aqueous solutions of benzene. They suggested that the detection of phenol and diphenyl which they observed only from solutions irradiated in the absence of oxygen, indicated the occurrence of a free-radical mechanism involving the intermediate formation of hydrogen atoms and hydroxyl radicals. Phung and Burton[99] have recently confirmed that diphenyl ($G = 1.22$) is only detected from air-free aqueous benzene solutions.

Two different mechanisms involving bond rupture and rearrangement were suggested by Gordon and Burton[100] to account for yields of gaseous products observed in the radiolysis of benzene.

Patrick and Burton[101] noted that the polymer from irradiated benzene had a $G = 0.75$ which was independent of intensity and total energy input, and they also observed that, while the average molecular weight of this polymer increased non-linearly with energy input, the double bond content of the polymer decreased. In explanation of these results they suggested that a fixed fraction of primarly excited benzene molecules are excited to a particular energy level, and then react to give polymer formation.

Recently Doumani et al.[102] examined more thoroughly the polymer from irradiated benzene, and in addition to diphenyl, they have identified phenyl cyclohexene, phenyl cyclohexadiene, bicyclic compounds in which neither ring is aromatic, hydrogenated terphenyls and other polymeric material.

Hentz and Burton[103] examined the radiolysis, by fast electrons, of toluene and other alkylated benzenes, and in order to account for the low G-value for gas production (~ 0.2), which they believe is somewhat smaller than might be expected for compounds with several substituent carbon atoms, they suggest that the energy originally imparted to the aliphatic part of the molecule migrates in large part to the ring, where it is dissipated with little chemical effect. They describe this as "Sponge-type" protection.

The protection afforded by the benzene ring to other irradiated compounds has previously been mentioned (see page 7).

The first attempt at radiochlorination of the benzene ring appears to have been made by Alyea[104] in 1930. He observed the formation of benzene hexachloride from benzene saturated with chlorine gas exposed to alpha-radiation from radon. The same system has recently been examined by Harmer[105] using gamma-rays, and G-values of the order of thousands, referring to molecules reacted, are reported. The product was observed to be several isomers of benzene hexachloride. The radiochlorination of toluene is reported by the same worker to occur less rapidly then the benzene reaction, most of the chlorine being utilised by addition to the ring, although substitution was also observed to occur. Harmer[105] made the interesting observation, that the addition of small amounts of benzyl chloride to benzene or toluene produced a marked inhibition of the reaction, and he reports that a similar effect is not observed in the analogous photochemical reaction.

The chlorination of benzene, photochemically or in the presence of peroxide initiators, is reported to be a free radical process, resulting in an almost quantitative yield of the addition product benzene hexachloride at room temperature, although some substitution is reported to occur at higher temperatures.[106] Normally nuclear substitution chlorination products of aromatic compounds are obtained by the use of metal catalysts, such as ferric chloride, to promote an ionic mechanism.[107]

In recent years, Calingaert[108] et al. have reported an interesting study of the iodine catalysed photochlorination of benzene. In addition to the substitution products, mono, di and trichlorobenzenes, and the addition product benzene hexachloride, they have isolated several isomeric tetra and pentachlorocyclohexenes arising by partial addition of chlorine to the benzene ring.

The photochemical chlorination of toluene, both gas and liquid, is reported to result in principally side chain chlorination[109]. Veijola[110] has observed that the side chain reaction can be suppressed by chlorinating toluene at -20°C in the presence of benzoyl peroxide, when toluene hexachloride is the principal product.

The first published observation that carbon tetrachloride could be used as a radical chlorinating agent appears to be that of Kharasch[111], in 1945, who reported that carbon tetrachloride reacted with 1-octene to yield 1, 1, 1, 3-tetrachlorononane in the presence of peroxide initiators.

$$CCl_4 + CH_2 = CHC_6H_{13} \longrightarrow CCl_3CH_2CHCl\,C_6H_{13}$$

Since then carbon tetrachloride has been observed to add to a large number of olefines[112]. Bowen and Rohatgi[113] have noted that in a solution of anthracene in carbon tetrachloride under ultra-violet light, trichloromethyl radicals and chlorine atoms are formed, and they suggest that addition of these two types of radicals occurs at the 9 and 10 positions in the

anthracene molecule. Very recently Zimin et al.[114] have reported the formation of benzotrichloride from a benzene-carbon tetrachloride solution irradiated with gamma rays.

Work on the irradiation of pure benzene, pure toluene, and carbon tetrachloride solutions of these compounds will now be described.

EXPERIMENTAL

The irradiation of benzene

Analar benzene (May and Baker) was further purified by shaking with concentrated sulphuric acid for 24 hours, washed thoroughly with water, then dried with anhydrous sodium sulphate followed by a fractional distillation. The first and last 10% portions of distillate were discarded N_{20}^{D} = 1.5010 (Lit. N_{20}^{D} = 1.5011).

A G.P.C. analysis showed the presence of less than 0.05% cyclohexane present as an impurity.

Approximately 1 litre of benzene was irradiated in a stoppered annular glass vessel for 92 hours at a dose rate of 3.3×10^{16} eV/cc/min.

The irradiated solution was pale green in colour. Upon removal of unchanged benzene by distillation, a thin film of a viscous brown oil having a sharp characteristic smell was left in the distillation flask. This oil was dissolved in a little toluene and a 0.05 ml. sample of the solution was analysed by G.P.C. Three peaks were obtained on the chromatogram corresponding, in order of elution, to toluene, an unidentified product, and diphenyl. Furthermore, a certain fraction of the injected sample was not eluted from the G.P.C. column, suggesting the presence of higher boiling polymeric material.

The toluene was removed by distillation and gentle heating of the residue under high vacuum conditions produced approximately 30 mgs of white crystalline sublimate, m.p. 68-69°C (Authentic diphenyl m.p. 71°C). The brilliant red colouration indicative of diphenyl[69] was produced when a few mgs of the crystalline material in concentrated sulphuric acid was shaken with 1 drop of benzal chloride.

The irradiation of equimolar solutions of benzene in carbon tetrachloride

Benzene and carbon tetrachloride were purified as described previously.

The solutions were prepared immediately prior to irradiation and different volumes were irradiated for different times. For example:

(i) 390 mls for 170 hours at a dose rate of 6.38×10^{16} eV/cc/min.

(ii) 940 mls for 164 hours at a dose rate of 2.68×10^{16} eV/cc/min.

(iii) 5 litres for 430 hours at an unspecified dose rate.

Phosgene was detected by smell from each of the irradiated solutions. Hydrogen chloride, chloroform and other products, as determined by G.P.C. analysis, were estimated as follows:

Estimation of Hydrogen chloride

20 ml portions of the irradiated solution were shaken with decinormal sodium hydroxide. The alkali layer was then extracted several times with water and back titrated with decinormal hydrochloric acid, using bromophenol blue as an indicator. In this technique, there exists the possibility that the sodium hydroxide will react with other irradiation products present in the 20 ml organic portion. From a consideration of the known reactions of the three classes of products identified from this sytem, viz. hydrocarbons, chlorinated hydrocarbons and compounds containing the $-CHCl_2$ or $-CCl_3$ group, it is believed that the latter class alone might be susceptible to hydrolysis by alkali, but whether hydrolysis would occur with decinormal sodium hydroxide in the cold is not yet certain. Control experiments will be necessary to clarify this question.

Results for the hydrogen chloride content of the three solutions (i), (ii) and (iii) are listed on the following page:

	Moles of HCl	G-value
(i)	1.372×10^{-2}	3.1
(ii)	1.729×10^{-2}	3.8
(iii)	1.454×10^{-1}	-

Estimation of chloroform

A 250 ml portion of the irradiated solution was shaken thoroughly with water to remove hydrogen chloride then dried with anhydrous sodium sulphate. The filtered solution was then fractionally distilled, using a heated 4 feet glass column of 1 inch diameter packed with Stedman stainless steel gauze rings, and attached to a still-head with an adjustable liquid take-off system. Fractions were removed slowly, until the chloroform content of the collected fraction, as determined by G.P.C. analysis, was neglible. The chloroform content of the combined chloroform-containing fractions was then determined. The results are listed below: for the three solutions (i), (ii) and (iii):

	Moles of chloroform	G-value
(i)	1.676×10^{-3}	0.4
(ii)	2.128×10^{-3}	0.5
(iii)	2.010×10^{-2}	-

Determination of other irradiation products

The products were only determined qualitatively, and since essentially similar methods were applied to the three solutions (i), (ii) and (iii), only solution (iii) (5 litres of equimolar solution) will be considered to illustrate completely the general techniques used. It may be emphasized at this point, that many of the identifications depend on G.P.C. evidence alone, although it was possible in some cases to confirm identity by other means as given below.

Unchanged carbon tetrachloride and benzene were removed by distillation,

and during this process a white crystalline sublimate collected in the water condenser. This was removed with a little 40/60 petrol ether, recrystallised from aqueous alcohol, and identified as hexachlorethane by the methods already outlined for the identification of this compound (see page 33). The removal of unchanged starting material was completed by distillation under reduced pressure using a smaller flask attached to a short Vigreux fractionating column. The last fraction from this distillation was analysed by G.P.C.

Fraction: 3 gms of very pale yellow liquid OBT 80-100°C/60 mm.

Three peaks were obtained on the chromatogram corresponding, in order of elution, to benzene, an unidentified compound, and a small quantity of chlorobenzene.

The residual product (35 gms of a dark yellow viscous oil) was then fractionally distilled under low pressure conditions into four fractions:

Fraction I	3.0 gms of a white crystalline solid	OBT 40-60°C/10^{-1} mm.
Fraction II	5.5 gms of pale yellow liquid	OBT 60-90°C/10^{-3} mm.
Fraction III	7.0 gms of yellow viscous oil	OBT 90-140°C/10^{-3} mm.
Fraction IV	6.5 gms of brown very viscous oil	OBT 140-200°C/10^{-3} mm.

The residue was 9.5 gms of a black tar soluble in benzene. That the higher fractions were decomposing upon heating, was shown by the large quantity of hydrogen chloride detected in the cold trap at the end of the distillation.

By the methods described on page 33 fraction I was shown to be hexachlorethane.

A G.P.C. analysis of fractions II and III showed the presence of the same components but in different proportions. The peaks on the chromatogram were identified, in order of elution from the column, as:

(1) Unidentified compound (minor product)

(2) Hexachlorethane (major product)

(3) Unidentified compound (minor product)

(4) Benzal chloride (minor product)

(5) Benzotrichloride (major product)

(6) Unidentified compound (major product)

(7) Diphenyl (major product)

(8) Higher boiling material (major product)

Fraction IV was shown by G.P.C. analysis to contain diphenyl and higher boiling polymer material, most of which was not eluted from the column. In fact some decomposition occurred in the column, with the liberation of hydrogen chloride. This fraction was not investigated further.

Examination of fractions II and III.

Repeated fractional distillation under low pressure conditions did not markedly improve the separation of these fractions into pure components, and therefore they were combined together, dissolved in 60/80 petrol ether, and percolated slowly through an alumina column, using initially 60/80 petrol ether as the eluting solvent, and gradually adding benzene to increase the eluting power. 150 ml fractions were collected and the solvent distilled off. Fractions were obtained as shown below:

Fraction (1) : 2.4 gms pale yellow liquid

Fraction (2) : 2.1 gms pale yellow liquid

Fraction (3) : 1.4 gms colourless liquid

Fraction (4) : 0.8 gms colourless liquid

Fraction (5) : 0.5 gms colourless liquid

Fraction (6) : 0.3 gms yellow liquid

Fraction (7) : 0.2 gms yellow liquid

Another 10 fractions were collected and in each case only a small quantity of yellow oil was obtained. In addition a small quantity of white crystalline solid

material was obtained with each liquid fraction.

A G.P.C. analysis of each fraction indicated that only a partial separation had been achieved, although the products indicated by peaks 1, 3, 4 and 5 (see page 89) were now confined to the first two fractions. The crystalline solid material (~ 0.5 gms) was removed by filtration, dried on filter paper, and recrystallised from aqueous ethanol with difficulty. Viewed through the microscope, the crystalline material appeared to be a mixture of different crystal forms and the melting point determination was very unsatisfactory. Two different G.P.C. methods were used to show that the solid material was a mixture of at least five components.

1st Method Examination of solid material from the alumina column

The solid was dissolved in a little toluene and analysed by G.P.C. using an alumina column packing heated to 410°C. The peaks on the chromatogram were shown to represent the following compounds:

(1) Toluene

(2) Tetrachlorethylene

(3) para-dichlorobenzene

(4) 1, 2, 4-trichlorobenzene

(5) diphenyl

It has already been mentioned (see page 25) that using alumina at 410°C as a column packing, peaks obtained on the chromatogram often represented decomposition products of the injected sample. Using the large-scale G.P.C. unit with an alumina packing at 140°C, it was possible to collect eluted fractions and identify them by infra-red spectroscopy. In this way tetrachlorethylene and 1, 2, 4-trichlorobenzene were shown to be the decomposition products from hexachlorethane and the hexachlorocyclohexane isomers respectively.

There is evidence, which will be discussed later, to suggest that 3, 4, 5, 6-tetrachlorocyclohexene-1 is a constituent of the solid fraction, and it is not unlikely that para-dichlorobenzene may represent the product from the decomposition of the tetrachlorocyclohexene on the alumina at 410°C. Unfortunately none of this compound was independently available to confirm this.

2nd Method Examination of the solid compound from the alumina column

In this case, the toluene solution of the solid material was analysed using a 25% silicone oil-Celite column packing heated to 120°C. The following compounds were identified:

(1) Toluene

(2) Hexachlorethane

(3) Unidentified compound

(4) Diphenyl

It was shown that none of the hexachlorocyclohexane isomers were eluted from this column packing. The unidentified compound is believed to represent a hydrocarbon for it has the same retention time on the G.P.C. column as the unidentified product from irradiated benzene.

To summarise, by a combination of two different G.P.C. methods, the solid material obtained from the alumina separation was shown to be a mixture of:

(1) Hexachlorethane

(2) Diphenyl

(3) Hexachlorocyclohexane

(4) A compound believed to be tetrachlorocyclohexene

(5) A compound believed to be a hydrocarbon

Examination of the liquid fractions from the alumina column (see page 89).

The two G.P.C. methods already described were applied to the liquid fractions. The products shown to be constituents of the solid fraction were present in all the fractions together with unidentified high boiling compounds. In addition benzal chloride (small quantity) and benzotrichloride were present in the first two fractions.

The addition of concentrated sulphuric acid to one drop of either of the first two fractions resulted in the formation of a brilliant red colour - the characteristic colour test for diphenyl in the presence of benzal chloride.[69]

It is worth while noting at this point, that some of the sterio hexachlorocyclohexane isomers, and the 3, 4, 5, 6-tetrachlorocyclohexene-1 isomers are recorded in the literature as liquids which crystallise only with difficulty to form low melting point solids.[108]

The infra-red spectrum of fraction I from the alumina separation column

This fraction was obtained as 2.4 gms of pale yellow liquid (see page 89).

An infra-red report from Harwell confirmed the presence of benzotrichloride and hexachlorethane. Benzal chloride and diphenyl, shown to be present in trace quantities by G.P.C., were not detected in the infra-red spectrum. The report also assigned certain strong absorptions near 3060 cm^{-1} to = CH groups of cyclic origin, and suggested therefore that a partly chlorinated cyclohexene was present in the fraction.

The spectrum of the same fraction was obtained in this department along with that of hexachlorethane and benzotrichloride, for comparison with the spectra of the 3, 4, 5, 6-tetrachlorocyclohexenes, studied by Orloff et al.[108] and the spectra of 1, 2, 3, 4, 5, 6-hexachlorocyclohexanes, studied by Wollrab

and Meschka[115]. The two absorption bonds for hexachlorethane and most of the strong bands for benzotrichloride were readily detected in the spectrum of the irradiation fraction. The following table will demonstrate this:

Hexachlorethane (cm^{-1})	Benzotrichloride (cm^{-1})	Irradiation fraction (cm^{-1})
	3075	3078
	1450	1448
	1193	1194
	1185	-
	806	801
783	-	785
	725	732
	708	705
671	-	680

However Orloff et al.[108] have only published small diagrams of the spectra of the tetrachlorocyclohexenes without quoting any figures, and therefore no definite conclusions were obtained regarding the presence of these isomers in the irradiation fraction.

A cautious attitude was adopted regarding confirmatory evidence from the infra-red spectrum for the presence of hexachlorocyclohexanes, for Wollrak and Meschka[115] have published the spectra of five sterio isomers which all have a different spectrum pattern. All that can be safely said is that some of the strong absorptions observed for these isomers, especially the gamma-isomer, can be detected in the spectrum of the irradiation mixture.

Interpretation of the infra-red spectrum of a mixture is difficult,

because in such a spectrum, overlapping of bands due to the individual components will occur, and also it is not unlikely that frequency shifts will occur due to field influences of the components of the mixture. The spectrum of an equimolar mixture of benzal chloride and benzotrichloride was obtained but it was observed that frequency shifts were never greater than 4 cm^{-1}. (see infra-red tables).

The infra-red absorptions of all the compounds examined are listed in tables at the end of the thesis.

Chemical reactions of the irradiation fractions

Hydrolysis of the liquid fractions with 10% alcoholic potassium hydroxide, boric acid, or concentrated sulphuric acid, in an attempt to convert benzotrichloride into benzoic acid, merely yielded further complex solutions of products. Only after separation of the irradiation product mixture into less complex fractions has been achieved will it be possible to obtain confirmatory evidence for the presence of certain components by chemical reactions.

To summarise, from the irradiation of an equimolar solution of benzene in carbon tetrachloride, the following products have been identified:

(1) Chloroform

(2) Hydrogen chloride

(3) Hexachlorethane

(4) Chlorobenzene (small quantity)

(5) Benzal chloride (trace)

(6) Benzotrichloride

(7) Diphenyl

(8) Hexachlorocyclohexane

(9) Possibly tetrachlorcyclohexene.

In addition many higher boiling products remained unidentified.

It is believed that an efficient separation of some of the above products will only be achieved by irradiating large volumes of solution at a high dose rate, in order to obtain several hundred gms of product, which might be separated by vacuum rectification using a very efficient fractionating column, followed if necessary, by partititon chromotography. Orloff et al.[108] studied the iodine-catalysed photochlorination of benzene and they used these suggested techniques to obtain a partial separation of at least twelve products. They noted that large quantities of product were required for the technique to be at all successful.

The irradiation of a 5% (by volume) solution of benzene in carbon tetrachloride

Only a cursory description of this work will be given for the techniques adopted were similar to these already described for the equimolar benzene carbon tetrachloride solutions.

Two solutions were irradiated:

(1) 390 mls for 193 hours at a dose rate of 6.38×10^{16} eV/cc/min

(11) 4 litres for 165 hours at an unspecified dose rate

Hydrogen chloride results:

(1) 1.042×10^{-2} moles ($G = 2.1$)

(11) 7.241×10^{-2} moles

Chloroform was detected by G.P.C. analysis but not estimated quantitatively.

From solution (11) (4 litres), 25 mls of a very viscous dark yellow oil was obtained as product after removal of the unchanged benzene and carbon tetrachloride by distillation. In addition a large quantity of white crystalline

sublimate collected in the water condenser. This was identified as hexachlorethane by the previously described procedure (see page 33).

The 25 mls of oil decomposed, liberating hydrogen chloride, when it was molecularly distilled under low pressure conditions. Three fractions were obtained, although the bulk of the irradiation product was non-distillable dark brown tarry material.

Fraction I 3 mls of yellow oil OBT 80 - 100°C/10^{-4} mm.

Fraction II 1 ml of yellow oil OBT 100- 120°C/10^{-4} mm.

Fraction III 2 mls of very viscous oil OBT 160- 200°C/10^{-4} mm.

By employing the same G.P.C. methods described previously, the following products were identified in the first two fractions.

(1) Hexachlorethane

(2) Benzotrichloride (small quantity)

(3) Hexachlorocyclohexane

(4) Possibly tetrachlorocyclohexene

(5) Diphenyl (small quantity)

Fraction III gave only one small peak on the chromatogram corresponding to a trace of diphenyl. This fraction was redistilled and a chemical analysis suggested the empirical formula $C_5H_3Cl_4$

Analysis found		Analysis calculated for $C_5H_3Cl_4$	
C	29.4%	C	29.3%
H	1.7%	H	1.4%
Cl	69.2%	Cl	69.3%
Total	100.3		

The remainder of this fraction (1.3 mls) was refluxed with 10 mls of freshly prepared 10% alcoholic potassium hydroxide for 30 minutes, then

the reaction mixture was poured into water and shaken several times with chloroform. The chloroform extract, was dried with anhydrous sodium sulphate, then the chloroform was removed by distillation leaving a brown viscous oil which was molecularly distilled to produce one fraction:

Approximately 200 mgs of pale yellow oil OBT 75-90°C/10^{-4} mm.

A sodium fusion test gave a negative result for chlorine and a chemical analysis suggested the empirical formula $C_5H_3O_4$

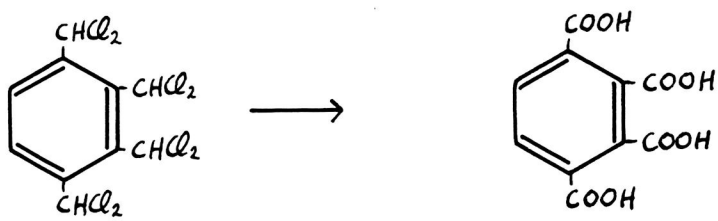
Analysis found		Analysis calculated for $C_5H_3O_4$	
C =	46.2%	C =	47.3%
H =	3.2%	H =	2.3%
Total	49.4	O =	50.4%

$\therefore$ O = 50.6%

The overall hydrolysis reaction may be written as:

$$C_5H_3Cl_4 \longrightarrow C_5H_3O_4$$

and this scheme may be accommodated by the following two compounds:



$$(C_5H_3Cl_4)_2 \longrightarrow (C_5H_3O_4)_2$$

So far no other evidence has been obtained to confirm such suggestions. Also, according to the above scheme, it might be expected that benzal chloride, rather than benzotrichloride would be detected in the lower boiling fractions. However, while a small quantity of the latter compound was detected, no

evidence for the presence of benzal chloride was obtained.

It may be noted at this point, that the corresponding higher boiling fraction from the irradiated equimolar benzene-carbon tetrachloride product mixture was not examined in the same way as the above fraction.

To summarise, in comparison with the results from the equimolar solution of benzene in carbon tetrachloride the same products, with the exception of chlorobenzene and benzal chloride, were detected although benzotrichloride and diphenyl, observed as major products from the equimolar solution, are present as minor components from the dilute solution. The major products are now hexachlorethane and higher boiling unidentified compounds, some of which readily decompose with loss of hydrogen chloride on heating.

The irradiation of toluene

B.P. Toluol supplied by J.F. Macfarlan was purified by shaking with portions of concentrated sulphuric acid until no yellow colour formation was observed in the acid layer. It was then washed thoroughly with water, dried with anhydrous sodium sulphate and fractionally distilled under reduced pressure. The first and last 10% portions of the distillate were discarded.

$$N^{D}_{20} = 1.4968 \qquad (\text{Lit. } N^{D}_{20} = 1.4963)$$

No impurities were detected by a G.P.C. analysis.

435 mls of pure toluene were irradiated in a stoppered annular glass vessel for 143 hours at a dose rate of 6.86×10^{16} eV/cc/min.

The irradiated solution was pale-green in colour. Upon removal of

the unchanged toluene by distillation under reduced pressure, a film of a brown viscous oil remained in the distillation flask. The same characteristic sharp smell encountered from the irradiated benzene product was evident and the oil exhibited a bright-blue fluorescence in ultra-violet light. This suggested the presence of stilbene as a reaction product.

A G.P.C. analysis of the oil showed the presence of at least seven irradiation products, although some of the peaks on the chromatogram were incompletely resolved. Dibenzyl was shown to be the major product and stilbene was present in trace quantity.

The compound 4-methyl diphenyl methane was considered as a possible reaction product and was synthesised according to the method of Hirst and Cohen[116], from toluene and benzyl chloride in the presence of an aluminium - mercury couple. However this synthesis was not entirely satisfactory. The product mixture was fractionally distilled as recommended into a number of fractions whose composition was tested by a G.P.C. analysis. Dibenzyl and stilbene were produced from the reaction in addition to other unidentified products. The major reaction product from the synthesis was a black tar. All that can safely be said is that an examination of the chromatograms of the different fractions obtained from this synthesis, showed that the major peak on the chromatogram, which is assumed to represent 4-methyl diphenyl methane, had a retention time corresponding to a peak on the chromatogram of the irradiated toluene product mixture. It would probably be easier to synthesise this compound by reduction of 4-methyl benzophenone, although reduction of benzophenones is known to give small yields of product.

To summarise, the irradiation of toluene produces dibenzyl, stilbene (trace), possibly 4-methyl diphenyl methane and at least four other unidentified

products. 4, 4'- dimethyl diphenyl is not an unlikely product and the synthesis of this compound by the Ullman reaction[117] from para-iodo toluene and finely divided copper deserves to be carried out.

The irradiation of equimolar toluene-carbon tetrachloride solutions

Toluene and carbon tetrachloride were purified as described for previous work, and equimolar solutions were prepared immediately prior to irradiation.

Two different volumes of solution were irradiated for different times:

(I) 390 mls for 122 hours at a dose rate of 6.38×10^{16} eV/cc/min

(II) 5 litres for 500 hours at an unspecified dose rate.

Hydrogen chloride and chloroform were estimated as previously described for the benzene-carbon tetrachloride work. The results obtained were:

Solution	Moles of HCl	G-value (HCl)	Moles of $CHCl_3$	G-value ($CHCl_3$)
(I)	1.372×10^{-2}	4.2	4.910×10^{-3}	1.5
(II)	2.417×10^{-1}	-	9.942×10^{-2}	-

It should be noted that the above experiments have not been repeated for reproducibility.

Determination of other reaction products

The techniques applied to the two solutions were similar and details of the 5 litres experiment will be given.

Upon removal of unchanged toluene and carbon tetrachloride by distillation under reduced pressure, 51 gms of a dark brown solution was obtained as residual product. In addition a white crystalline sublimate collected in the water condenser. This was identified by the previously described

methods (see page 33) as hexachlorethane. The residual solution was distilled under reduced pressure in a flask attached to a short Vigreux fractionating column and two liquid fractions were collected using only the water pump:

Fraction I : Pale yellow liquid OBT 120-130°C/40 mm.

Fraction II : Pale yellow liquid OBT 130-150°C/40 mm.

The residual oil (40 gms) was then fractionally distilled under low pressure conditions.

Fraction III : Pale yellow oil OBT 90-95°C/10^{-3} mm.

Fraction IV : Colourless liquid OBT 95-120°C/10^{-3} mm.

Fraction V : Colourless liquid OBT 120-130°C/10^{-3} mm.

Fraction VI : Yellow liquid + a white crystalline solid OBT 130-150°C/10^{-3} mm.

Fraction VII : White crystalline solid OBT 150-175°C/10^{-3} mm.

At this point the very viscous yellow-brown oil left in the distillation flask was transferred to a molecular cup-still apparatus and distilled under low pressure conditions.

Fraction VIII : Viscous yellow oil OBT 150-175°C/10^{-4} mm.

Fraction IX : Very viscous yellow-brown oil OBT 175-210°C/10^{-4} mm.

An almost solid brown oil (10.5 gms) remained in the distillation flask.

Examination of fractions I and II

A G.P.C. analysis showed the presence of the following products in both fractions:

(1) Toluene (trace)

(2) Hexachlorethane

(3) Chlorotoluenes (8.590×10^{-3} moles)

(4) Benzyl chloride (1.301×10^{-2} moles)

The identity of the products was confirmed by comparison of the infra-red spectra of the fractions with those of the above products. (refer to infra-red tables).

It has not yet been possible to obtain a separate estimation of the relative proportions of the three chloro-toluene isomers. In the infra-red spectra of the product fractions the main regions where differntiation is possible viz. 2000-1660 cm^{-1} and 850-700 cm^{-1}, are obscured by strong absorptions in the same regions by other components.

Examination of fractions III, IV and V.

These fractions were shown by G.P.C. analyses to contain the following compounds present in different proportions in each fraction:

(1) Hexachlorethane

(2) Unidentified product (trace)

(3) Para-methyl benzal chloride (small quantity)

(4) A compound believed to be benzyl chloroform (large quantity)

(5) Para-methyl benzotrichloride

(6) Hydrocarbon products from irradiated toluene alone, for example, dibenzyl (large quantity), 4-methyl diphenyl methane (small quantity) and stilbene (trace).

In order to obtain the above identifications, para-methyl benzal chloride, para-methyl benzotrichloride, and benzyl chloroform were synthesised (see pages 105-106). However the synthesis of benzyl chloroform was not satisfactory and this identification was not conclusive (see page 107).

Fractions IV and V were combined together and passed through the large-scale G.P.C. separation column, and a fraction was obtained (1.5 mls) containing only the compounds believed to be benzyl chloroform and para-methyl benzotrichloride.

Fraction obtained from G.P.C. column N_{20}^{D} = 1.5510

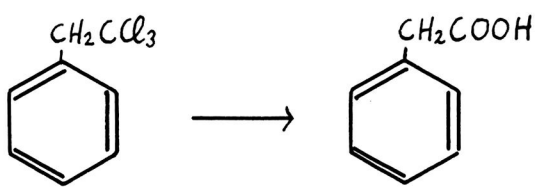
Synthesised para-methyl benzotrichloride N_{20}^{D} = 1.5500

A chemical analysis suggested the empirical formula $C_8H_7Cl_3$, which is that of benzyl chloroform and para-methyl benzotrichloride.

Analysis found		Analysis calculated for $C_8H_7Cl_3$	
C	46.2%	C	45.8%
H	3.6%	H	3.4%
Cl	50.2%	Cl	50.8%
Total	100.0		

Hydrolysis of the fraction collected from the G.P.C. column

0.5 ml of this fraction was refluxed with 5 mls of freshly prepared 10% alcoholic potassium hydroxide for 30 minutes. The reaction solution was then poured into 40 mls of water and the ether extract, after being dried with anhydrous sodium sulphate, was distilled to remove the ether, leaving a small quantity of a yellow oil. This oil was dissolved in a little 40/60 petrol ether and upon standing for a few days crystals appeared in the solution. These needle-shaped crystals were removed by filtration (m.p. = 73-75°C, accompanied by slight sublimation). Insufficient material was obtained for analysis. The following hydrolysis may have been effected:



(m.p. 78°C.)

Examination of the infra-red spectrum of the fraction from the G.P.C. column

A comparison of the infra-red spectrum of this fraction with that of para-methyl benzotrichloride, revealed the presence of several absorption bands which appear to be characteristic of the latter compound and which had the correct intensity distribution (see infra-red tables). In addition, there were other strong absorption bands observed in the spectrum of the radiation fraction which may be assigned to benzyl chloroform. This can only be confirmed when a more satisfactory method of synthesis is devised to obtain pure benzyl chloroform.

Examination of the crystalline solid obtained from fractions VI and VII (see page 101).

The solid present in fraction VI was removed by filtration, combined with fraction VII and recrystallised from aqueous ethanol m.p. 51-52°C. (Authentic dibenzyl m.p. 52°C).

A comparison of an X-ray powder photograph of the solid material with that of dibenzyl showed no differences.

A chemical analysis was also obtained:

Analysis found		Analysis calculated for $C_{14}H_{14}$	
C :	92.1%	C :	92.3%
H :	7.8%	H :	7.7%
Total	99.9%		

Approximately 5 gms of this crystalline product were obtained.

G.P.C. analyses have shown that dibenzyl is also present, dissolved in liquid fractions IV, V and VI (see page 101).

Examination of fractions VIII and IX (see page 101).

No information was obtained concerning these fractions by G.P.C.

means. Oxidation using alkaline potassium permanganate, hydrolysis using alcoholic potassium hydroxide, hydrolysis using water at 180°C in a Carius tube and bromination using bromine in carbon tetrachloride, are some of the chemical tests which were applied to these fractions. It is considered that each fraction contains too many components for identification by chemical or infra-red means and of course only small quantities of each fraction were available.

Preparation of para-methyl benzal chloride and para-methyl benzotrichloride

The combined synthesis was a modification of Gattermann's synthesis of para-methyl benzyl chloride alone.[118]

48 gms of phosphorus pentachloride were added slowly to 20 gms of para-tolyl aldehyde, then the dark brown reaction mixture was kept at a temperature of 90°C for 2 hours in a fume cupboard with a tube containing calcium chloride attached to the open end of the reaction flask. The reaction mixture was allowed to cool then poured into a mixture of ice and water from which the organic products were extracted with ether. Upon removal of the ether by distillation, 30 mls of a pale yellow viscous liquid were obtained. A fractional distillation of this product under reduced pressure produced three fractions:

Fraction I :	1 ml of a colourless liquid	OBT 90-125°C/40 mm.
Fraction II :	25 mls of a colourless viscous liquid	OBT 140-150°C/30 mm.
Fraction III :	1 ml of a yellow viscous liquid	OBT 160-200°C/30 mm.

Fraction II was placed in a refrigerator overnight and a mass of crystalline material came out of solution. This was removed by filtration. Although the freezing process was repeated several times, the liquid as indicated by a G.P.C. analysis still contained some solid material in solution. Accordingly the solution was passed through the large-scale G.P.C.

separation column and a fraction was obtained (1 ml) containing no dissolved solid.

The solid material (15 gms) was recrystallised from aqueous alcohol m.p. = 45-46°C (Authentic p-methyl benzal chloride m.p.=47°C). A chemical analysis was obtained:

Analysis found		Analysis calculated for $C_8H_8Cl_2$	
C :	54.7%	C :	54.9%
H :	4.6%	H :	4.6%
Cl :	40.3%	Cl :	40.5%
Total	99.6		

A chemical analysis of the liquid fraction suggested the empirical formula $C_8H_7Cl_3$, which is that of methyl benzotrichloride.

Analysis found		Analysis calculated for $C_8H_7Cl_3$	
C :	46.1%	C :	45.8%
H :	3.2%	H :	3.4%
Cl :	50.5%	Cl :	50.8%
Total	99.8%		

Preparation of benzyl chloroform $C_6H_5CH_2CCl_3$

The procedure adopted was a modification of the synthesis of benzyl methylene chloride described by Auwers and Kiel.[119]

40 gms of phosphorus pentachloride were added slowly to 20 gms of freshly distilled phenyl acetaldehyde dissolved in a mixture of 50 mls of 80/100 petrol ether plus 5 mls of analar benzene. The dark brown reaction mixture was kept at a temperature of 90°C for 1 hour in a fume cupboard with

a tube containing calcium chloride attached to the open end of the reaction flask. Thereafter the procedure was as described by Auwers and Kiel. The 10 gms of pale yellow viscous oil obtained as product was fractionally distilled under low pressure conditions to yield two fractions:

Fraction I : 6 mls of pale yellow liquid OBT 80-100°C/10^{-4} mm.

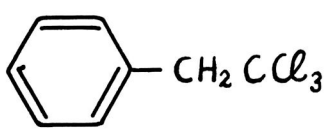
Fraction II : Yellow viscous liquid OBT 120-160°C/10^{-4} mm.

A G.P.C. analysis of the first fraction showed the presence of two components which were incompletely resolved on the chromatogram. It was possible by the use of the large-scale G.P.C. separation column to obtain a pure fraction (0.5 mls) of the component represented by the first peak. A chemical analysis of this pure fraction was obtained.

Analysis found		Analysis calculated for $C_8H_8Cl_2$	
		i.e. $C_6H_5CH_2CHCl_2$	
C :	45.6%	C :	45.8%
H :	3.2%	H :	3.4%
Cl :	49.9%	Cl :	50.8%
Total	98.7		

The second component of fraction I above was not obtained pure. However its retention time on the G.P.C. chromatogram corresponded to that of the compound represented by peak 4 (page 102) on the chromatogram of the products from the irradiated toluene-carbon tetrachloride solution. By analogy with the synthesis of para-methyl benzotrichloride, the second component is believedto represent benzyl chloroform.

viz.



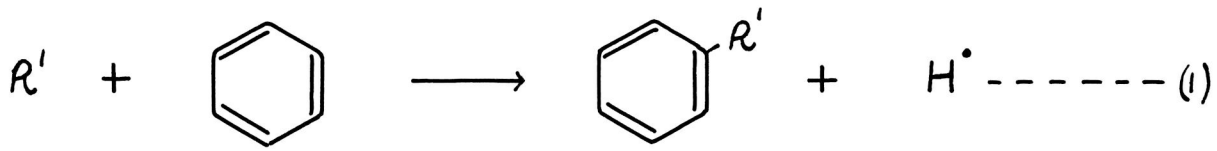
DISCUSSION

The irradiation of benzene and toluene

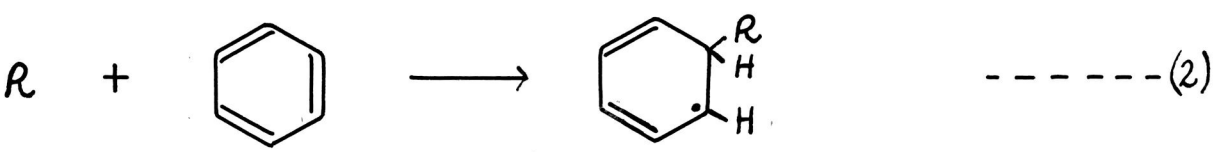
The formation of diphenyl from irradiated benzene may be accommodated in a scheme involving an initial splitting of the carbon-hydrogen bond, followed by dimerisation of the phenyl radicals to form diphenyl. The other expected dimerisation product, hydrogen gas, has been detected in small yield (G = 0.04) by previous workers.[98]

However such a simple scheme fails to account for the formation of higher boiling polymeric material, nor does it account for the products identified by recent workers[102] (see page 82). Patrick and Burton[101] suggest that certain excited benzene molecules react with any available free radicals, for example, phenyl radicals or hydrogen atoms, to give a free radical polymer whose growth is ultimately terminated by combination with another free radical.

A short chain process involving the initial attack of primary radicals on benzene molecules may occur by the following processes, where R' represents a phenyl radical, and R a phenyl radical or a hydrogen atom:



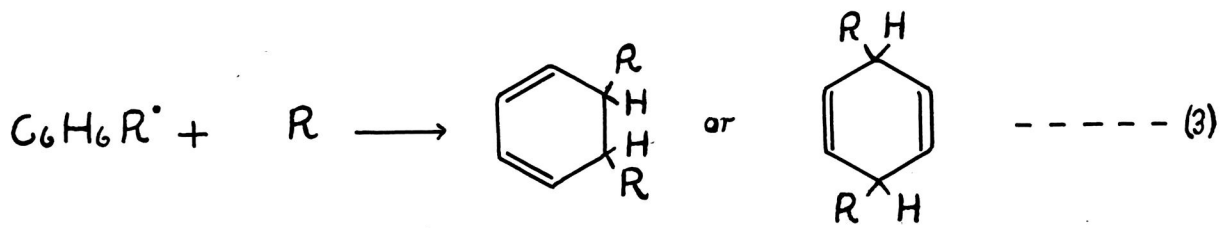
(1)



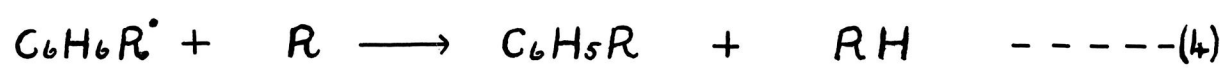
(2)

Reaction (I) was proposed by Grieve and Hey[120] to account for the formation of substituted diphenyls and polyphenyls when benzoyl peroxide is decomposed in an aromatic solvent. This reaction involving the splitting of a C-H bond may be strongly endothermic, and Hine[121] has pointed out that such a reaction will have too high an activation energy to occur fast enough to compete with other processes such as the dimerisation of two phenyl radicals. The difficulty of removing an aromatic hydrogen is also manifested by the radical chlorination of benzene which yields the addition product benzene hexachloride ($C_6H_6Cl_6$) in almost 100% yield at ordinary temperatures.[106]

Consider reaction (2). The cyclohexadienyl radical may react further with radicals yielding, either an addition product (3), or a substitution product (4) as a result of a hydrogen abstraction reaction:



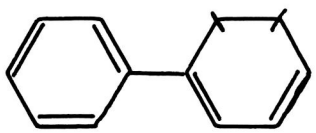
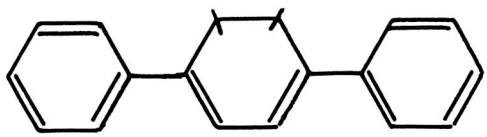
----- (3)



----- (4)

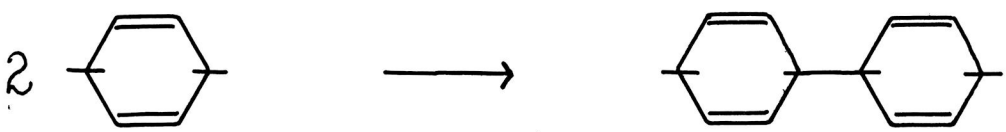
Such products as would be obtained from (3) have been reported by Stockmayer and Peebles[122] and by Marvel and Anderson[123]. These workers demonstrated that growing polymeric radicals may be added to aromatic hydrocarbons, the products of such reactions being co-polymers which incorporate the aromatic compounds in their chains.

The occurrence of reaction (3) in the irradiated benzene system, depending on whether R was a hydrogen atom or a phenyl radical, would give rise to (i) cyclohexadiene, (ii) phenyl cyclohexadiene, and (iii) a partially hydrogenated terphenyl:

(i)  (ii)  (iii) 

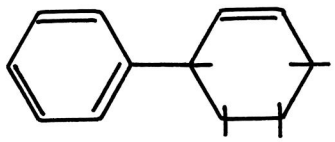
(ii) and (iii) have been observed by Doumani et al.[102] from the radiolysis of benzene.

The formation of bicyclic compounds in which neither ring is aromatic, (observed by Doumani et al.) may be considered in terms of a dimerisation reaction involving two cyclohexadienyl radicals (formed from reaction (2) when R represents a hydrogen atom):



Although reaction (4) may contribute to the formation of diphenyl, when R is a phenyl radical, its importance when R is a hydrogen atom must

be very slight for only a small yield of hydrogen gas has been observed.[98] There of course exists the possibility that hydrogen gas, as it is formed, reacts with the highly reactive intermediate cyclohexadienyl radicals. The presence of phenyl cyclohexene (iv), detected

(iv) 

by Doumani et al,[102] can be explained by such a process. However it is believed that the major process occurring in the radiolysis of benzene is the addition of hydrogen atoms and phenyl radicals to the benzene ring, followed by the processes discussed. Doumani et al.[102] prefer an excited molecule theory and biradical formation to explain their results.

In the radiolysis of toluene, dibenzyl was observed as a major product, and stilbene and 4-methyl diphenyl methane as minor components. In addition there were unidentified products and polymeric material.

It is to be expected that an initial carbon-hydrogen bond split will result in the formation of hydrogen atoms and benzyl radicals, which may either dimerise (i), or react with toluene molecules (ii) to form dibenzyl:

(i) $C_6H_5CH_2^{\bullet} + C_6H_5CH_2^{\bullet} \longrightarrow C_6H_5CH_2CH_2C_6H_5$

(ii) $C_6H_5CH_2^{\bullet} + C_6H_5CH_3 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + H^{\bullet}$

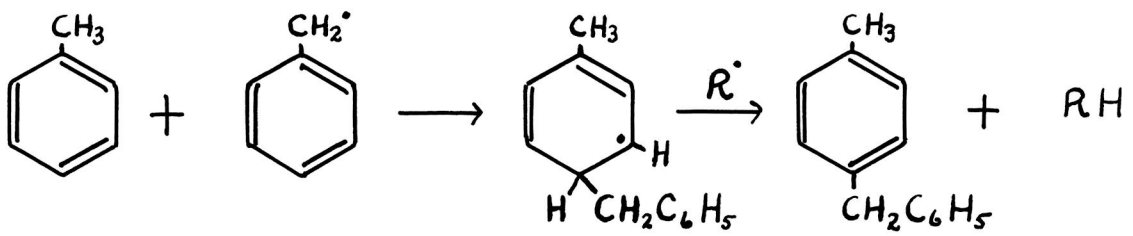
A similar reaction scheme explains the formation of 4, 4'- dimethyl dibenzyl from an irradiated carbon tetrachloride - para-xylene solution.[46]

The low observed yield of hydrogen gas (G = 0.09)[98], points to the occurrence of a reduction reaction, involving the addition of hydrogen atoms to the aromatic nucleus, similar to the reactions postulated for the benzene work. However, the intermediate products from irradiated toluene, shown by the number of peaks on the G.P.C. chromatogram, have not yet been identified.

It is difficult to account for the formation of stilbene (observed in trace quantity), unless it is assumed that an elimination reaction involving two reactive benzyl radicals may occur occasionally:

$$2\ C_6H_5CH_2^{\bullet} \longrightarrow C_6H_5CH = CH\ C_6H_5 + H_2$$

The third reaction product, 4-methyl diphenyl methane, is believed to occur from a reaction involving a benzyl radical and toluene, analogous to that involving a phenyl radical and a benzene molecule:



followed by hydrogen atom abstraction of the intermediate radical by any of the initially formed radicals (R). Although this reaction may result in the formation of the ortho, meta and para benzyl substituted intermediate radicals, each of which, upon hydrogen atom abstraction, would give rise

to an isomeric product, only the one product has been observed.

The polymeric material is believed to arise by a scheme similar to that discussed for the irradiated benzene polymer.

The irradiation of benzene - carbon tetrachloride solutions

The radiolysis of carbon tetrachloride is taken to result in the formation of chlorine atoms and trichloromethyl radicals, (see page 48) followed

$$CCl_4 \longrightarrow CCl_3^{\bullet} + Cl^{\bullet}$$

by dimerisation reactions yielding hexachlorethane and chlorine gas.

The study of the products from the irradiation of solutions of benzene in carbon tetrachloride, has shown that three types of reactions appear to be involved:

(1) Chlorination of the hydrocarbon by chlorine atoms

(2) Reactions involving trichloromethyl radicals.

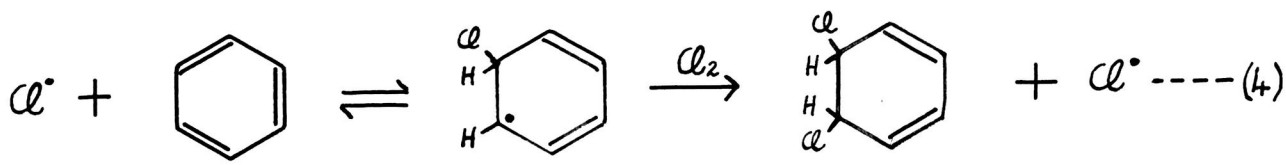
(3) Reactions involving only the hydrocarbon.

The chlorination products were chlorobenzene and tetrachlorocyclohexene as minor components and hexachlorocyclohexane.

Noyes et al.[124] suggested that chlorine atom attack on benzene is a termolecular process:

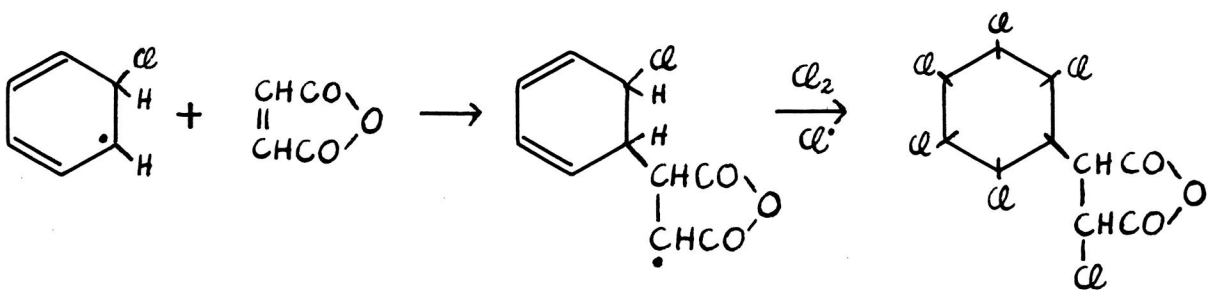
$$Cl^{\bullet} + Cl_2 + C_6H_6 \longrightarrow C_6H_6Cl_2 + Cl^{\bullet}$$

However Walling[125] has pointed out that a reversible addition yields the same kinetics,



and is plausible because of the high resonance energy of the aromatic ring being attacked. This reaction was also proposed by Levy et al.[126] for the reaction between benzene and methyl radicals. Process (4) is favoured to account for the irradiation products tetrachlorocyclohexene and hexachlorocyclohexane. The dichloro product from reaction (4) has not been observed but it is believed that further attack of chlorine on the cyclohexadiene would result in the formation of the tetra and hexachloro products. Recent workers[108] obtained the tetrachlorcyclohexene from the iodine catalysed photochlorination of benzene and showed that this compound, (which they identified as a mixture of four stereoisomers of 3, 4, 5, 6-tetrachlorocyclohexene-1), reacted rapidly with chlorine on illumination to form the stereoisomeric hexachlorocyclohexanes.

Qualitative evidence that reaction (4) occurs, has been furnished by Ecke et al.[127], who noted that when benzene and maleic anhydride were chlorinated together in the presence of light, a reaction occurred leading to phenyl chloro succinic anhydride together with some pentachlorocyclohexyl succinic anhydride, apparently via a sequence such as:



So far only the addition products from an irradiated benzene-carbon tetrachloride solution have been discussed. Consider now the following substitution products:

(1) hydrogen chloride

(2) chloroform

(3) chlorobenzene

(4) benzotrichloride

(5) benzal chloride

Hydrogen chloride formation is not explained by reaction (4), which may therefore be competing with a reaction such as:

$$Cl^{\bullet} + C_6H_6 \longrightarrow C_6H_5^{\bullet} + HCl$$

which has been postulated as the chain propagation step in the high temperature vapour phase halogenation of benzene.[128] However it is postulated that the effective reaction for the formation of hydrogen chloride is a similar abstraction reaction, involving a carbon tetrachloride molecule and a hydrogen atom:

$$CCl_4 + H^{\bullet} \longrightarrow CCl_3^{\bullet} + HCl$$

This mechanism is believed to be more important than the alternative scheme:

$$CCl_4 + H^{\bullet} \longrightarrow Cl^{\bullet} + CHCl_3$$

for there is a ten-fold difference in the observed G-values of the two products, hydrogen chloride and chloroform. Also, arguing on thermochemical grounds, from a consideration of the bond dissociation energies involved, the former reaction is more exothermic than the latter reaction by approximately 10 K.cals/mole.

In addition to the normal dimerisation reactions (for example a

phenyl radical plus a trichloromethyl radical giving rise to benzotrichloride), a number of reactions may be considered to account for the formation of chlorobenzene and benzotrichloride. For example:

$$C_6H_6 + CCl_3^{\bullet} \longrightarrow C_6H_5CCl_3 + H^{\bullet} \qquad \text{-----(5)}$$

$$C_6H_6 + CCl_3^{\bullet} \longrightarrow C_6H_5^{\bullet} + CHCl_3 \qquad \text{-----(6)}$$

$$C_6H_5^{\bullet} + CCl_4 \longrightarrow C_6H_5CCl_3 + Cl^{\bullet} \qquad \text{-----(7)}$$

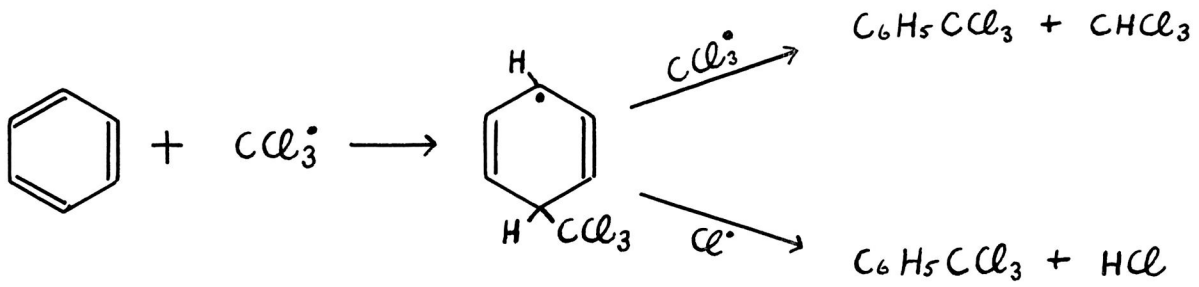
$$C_6H_5^{\bullet} + CCl_4 \longrightarrow C_6H_5Cl + CCl_3^{\bullet} \qquad \text{-----(8)}$$

Reaction (5) may be strongly endothermic and it is unlikely that it will occur fast enough to compete with the dimerization reaction involving trichloromethyl radicals.

With regard to reaction (6), Kooyman[129], investigating the ability of trichloromethyl radicals to abstract hydrogen rather than add to an olefinic double bond, studied the retarding effect of benzene on the carbon tetrachloride-cetene-benzoyl peroxide reaction, and he observed that benzene was apparently unreactive towards the trichloromethyl radical. Reaction (6) is therefore unlikely.

Now if reactions (7) and (8) were equally probable, equal quantities of chlorobenzene and benzotrichloride would be formed. In fact chlorobenzene was a minor component and benzotrichloride a major product. It is unlikely that benzotrichloride arises from reaction (7) for the outcome of two alternative paths for a reaction is likely to be the formation of the most stable radical which in this case is believed to be the trichloromethyl radical.

A two stage version of reaction (6) is believed to be the most likely source of benzotrichloride, hydrogen chloride and chloroform:

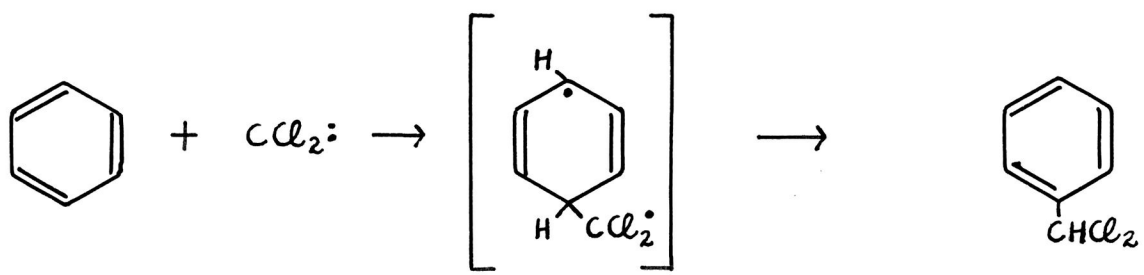


It is suggested that a similar reaction, involving a benzene molecule and chlorine atom, will preferentially follow the path set out in reaction (4) for the formation of benzene tetrachloride and benzene hexachloride.

The formation of benzal chloride (a minor product), is difficult to account for unless it is assumed that certain reactive trichloromethyl radicals decompose to form the dichloromethyl diradical and a chlorine atom:

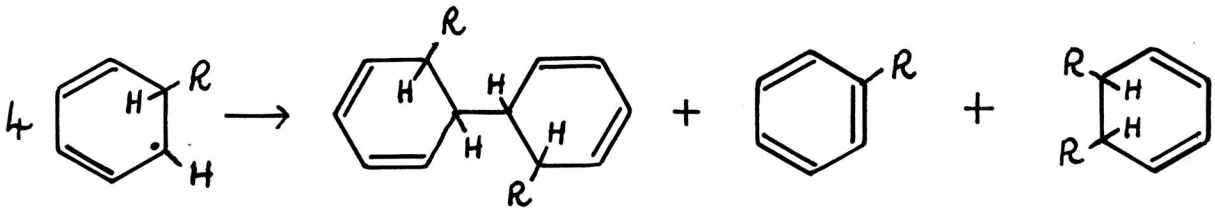
$$CCl_3^{\bullet} \longrightarrow CCl_2: + Cl^{\bullet}$$

Semeluk and Bernstein[73] have suggested that this reaction occurs during the thermal decomposition of chloroform. The biradical might then react directly with benzene to form benzal chloride, or alternatively it might form an unstable intermediate,



which would rapidly rearrange to give the stable benzal chloride.

The major product from the irradiated benzene-carbon tetrachloride solution was high boiling viscous oils in addition to a certain amount of tarry non-distillable material. Dannley et al.[130] have noted that in all free radical substitution reactions involving phenyl radicals, large quantities of tars are obtained. A similar observation was made by Walling[130] who suggests that the higher boiling products do not arise from successive radical attack upon stable aromatic molecules, but rather that highly reactive intermediate species are formed, perhaps through sequencies such as:



Further radical attack may then occur on the reactive cyclohexadiene molecule. It is perhaps more satisfactory to consider successive addition of radicals to the highly reactive intermediate cyclohexadienyl radical, which will result in the formation of substituted cyclohexanes, cyclohexenes and cyclohexadienes. It is not unreasonable to assume, that, depending on the extent of chlorine substitution, some of these poly substituted products may be unstable, and the loss of hydrogen chloride may occur on heating. It may be noted, that in the irradiation of a 5% solution of benzene in carbon tetrachloride, the higher boiling products decomposed upon heating

with the liberation of hydrogen chloride and a product was obtained which analysed for the substitution of four ($CHCl_2$) groups in a benzene ring.

The irradiation of toluene-carbon tetrachloride solutions

Most of the discussion on the benzene-carbon tetrachloride workalso applies to the toluene-carbon tetrachloride irradiation products.

The main difference observed in this work was the absence of nuclear chlorinated toluene addition products, comparable to the benzene tetrachloride and benzene hexachloride. In this case, chlorination of the side chain occurred to benzyl chloride, and perhaps surprisingly, a slightly less quantity of chlorotoluene. Free radical chlorination of toluene using photo-initiation or peroxide catalysts has been reported to give side chain substitution products, with some ring addition occurring concomitantly[109]. On the other hand, the formation of ring substitution products, for example chlorotoluene, is normally carried out in the presence of catalysts favouring an ionic mechanism.

The nuclear substituted products methyl benzotrichloride, and methyl benzalchloride, together with chloroform and hydrogen chloride, are assumed to arise by mechanisms similar to those proposed for the benzene-carbon tetrachloride solutions.

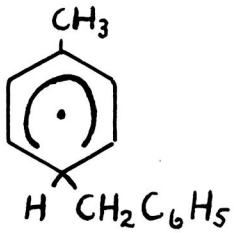
In addition the major product was benzyl chloroform which may arise either by attack of a benzyl radical on carbon tetrachloride, or attack of a trichloromethyl radical on toluene:

$$C_6H_5CH_2^{\bullet} + CCl_4 \longrightarrow C_6H_5CH_2CCl_3 + Cl^{\bullet} \qquad \text{-----(9)}$$

$$C_6H_5CH_3 + CCl_3^{\bullet} \longrightarrow C_6H_5CH_2CCL_3 + H^{\bullet} \qquad \text{-----(10)}$$

Kooyman[129] (see page 47) has also observed that toluene is only slightly reactive to trichlormethyl radicals and therefore reaction (9) is believed to be operative.

It is suggested, as in the benzene-carbon tetrachloride work, that the very high boiling compounds will be derived from addition of radicals to the intermediate radicals indicated by the aromatics isolated, for example:



As a number of radicals may add, it is not surprising that there is so much high boiling material of such an irresolvable character.

The mechanisms proposed have all been very tentative and it is readily admitted that most of the work requires to be repeated for a complete identification of products, followed by qualitative experiments to determine the relative importance of different reaction paths.

Above all it would appear to be desirable to irradiate a very low concentration of benzene in carbon tetrachloride, in which case direct effects of the gamma rays on the hydrocarbon would be negligible and information would be obtained regarding the attack of trichloromethyl

radicals and chlorine atoms on benzene molecules, rather than on a mixture of benzene molecules and benzene irradiation products.

INFRA RED SPECTRA

All values are given in wave numbers (cm^{-1}), and the intensity of vibration is indicated by very strong (vs), strong (s), medium (m) or weak (w).

a) Identification of a cracking product, obtained when gamma hexachlorocyclohexane was injected into the large-scale G.P.C. alumina column at 400°C, as 1, 2, 4-trichlorobenzene.

Cracking product		1, 2, 4-trichlorobenzene	
3100 m	1192 w	3100 m	1195 m
1880 w	1157 m	1880 w	1158 m
1735 w	1140 w	1740 w	1142 w
1570 vs	1122 vs	1572 vs	1122 s
1495 m	1095 s	1495 m	1095 s
1456 vs	1035 s	1455 vs	1035 s
1433 m	868 s	1434 m	865 s
1415 m	815 vs	1418 s	812 vs
1373 s	788 m	1375 s	788 m
1247 m	775 m	1248 m	774 m

b) Products from the irradiation of tetrachlorethylene shown to be (A) octachlorobutene-1 and (B) hexachlorobutadiene, the spectra of which is listed by Szatz and Sheppard[89].

Product A		Product B	
1642 m	810 m	1610 m	854 vs
1537 m	770 vs	1568 s	797 vs
1167 m	750 w	1172 s	777 s
960 w	742 w	1093 w	740 m
920 m		982 vs	720 w
850 w		944 s	647 s
835 s		890 w	

c) Product mixture from the irradiation of a toluene carbon tetrachloride solution containing benzyl chloroform and para-methyl benzotrichloride.

Product mixture		p-methyl benzotrichloride	
3080 w	1182 m	2930 s	1035 m
3045 m	1585 w	1620 s	935 m
2940 w	1082 s	1580 w	878 m
1960 w	1035 vs	1505 m	825 m
1890 w	1002 w	1458 s	805 vs
1810 w	948 vs	1390 m	750 vs
1610 m	920 m	1325 w	618 m
1590 w	875 m	1290 w	
1500 s	852 vs	1238 m	
1458 s	800 vs	1215 m	
1432 s	772 vs	1168 w	
1210 s	738 vs	1110 w	

d) Product mixture from the irradiation of a benzene carbon tetrachloride solution containing, benzotrichloride, hexachlorethane and possibly hexachlorocyclohexane[115] and tetrachlorocyclohexene[108].

Hexachlorethane

783 vs
671 m

Benzotrichloride

3075 m	872 s
1488 m	806 vs
1450 s	792 m
1193 s	765 w
1185 s	725 vs
1035 w	708 vs
1022 w	687 m

Product mixture

3087 s	1502 m	1106 s
3078 w	1479 vs	1086 m
2967 m	1449 w	1024 m
2945 m	1416 vs	1003 w
2878 w	1410 vs	975 s
1958 w	1369 w	936 s
1922 w	1319 m	919 s
1785 m	1292 w	907 m
1769 m	1271 w	381 vs
1736 w	1251 m	855 vs
1679 w	1214 m	802 vs
1659 w	1193 vs	785 s
1589 s	1183 vs	728 vs
1577 s	1161 s	703 s

Equimolar mixture of benzotrichloride and benzal chloride

3068 m	1075 w
3037 w	1032 w
1497 w	1001 w
1487 w	874 m
1450 s	840 m
1250 m	805 s
1212 m	795 m
1190 m	724 vs
1182 m	710 vs

Benzal Chloride

3075 m	1036 m
3037 m	1002 w
1496 m	872 w
1454 s	840 s
1251 s	795 w
1212 s	694 vs
1190 s	
1179 m	
1078 m	

e) Fraction from irradiated toluene-carbon tetrachloride solution, containing at least toluene, benzyl chloride, hexachlorethane and para-chloro toluene.

p-chloro toluene		benzyl chloride		irradiation fraction	
3080 s	1392 m	3060 s	1387 m	3064 s	1272 s
2985 s	1313 w	3038 s	1320 m	2976 s	1215 s
2926 s	1283 w	2984 s	1270 s	2900 m	1186 w
1908 m	1246 m	2892 m	1212 s	2761 w	1167 m
1792 m	1221 m	1958 m	1183 w	1961 m	1083 m
1738 m	1183 m	1888 m	1160 m	1896 m	1035 s
1644 m	1170 s	1805 w	1076 s	1817 w	1008 w
1612 m	1100 s	1765 w	1032 m	1778 m	962 s
1591 m	1050 m	1706 m	924 m	1712 s	930 w
1496 vs	1025 s	1608 m	814 s	1612 m	883 m
1460 vs	975 w	1590 m	765 s	1597 w	863 s
1448 s	946 m	1542 w	698 vs	1550 w	825 s
1412 s	804 vs	1498 s	676 s	1500 s	810 s
		1454 s		1458 s	780 s
				1385 m	702 s
				1320 w	685 s

GENERAL SUMMARY

Cobalt-60 has been used as a source of gamma ionising radiation and the induced chemical effects have been studied in the following classes of compounds: (i) chlorinated methanes (ii) allyl halides together with vinylidene chloride and tetrachlorethylene. (iii) Some aromatic hydrocarbons, alone, and in carbon tetrachloride.

A description is given of gas phase chromatography techniques which were developed to assist in the identification and quantitative separation of the irradiation products. X-ray and infra-red methods were also used where possible.

The products from the radiolysis of carbon tetrachloride, chloroform and methylene chloride have been determined and the yields of products have been expressed as G-values (number of molecules of product formed per 100 eV energy input). The results are consistent with reaction mechanisms involving homolysis of the C-Cl bond as the primary act, followed in the case of chloroform and methylene chloride by hydrogen atom abstraction by primary radicals. Thereafter, in each case, dimerisation of the free radicals is proposed as the predominant process. In addition, elimination reactions between certain radicals resulting in the formation of an unsaturated compound and hydrogen chloride have been considered. A scheme for the formation of unidentified C_3 and C_4 products is proposed. Finally the presence of dissolved oxygen was found to exercise an inhibiting effect upon the formation of certain products and this effect is discussed.

Vinylidene chloride was observed to polymerise readily with an almost 100% conversion to a solid polymer similar to that previously reported from benzoyl peroxide initiated polymerisation. Tetrachloroethylene was more resistant to radiation (G = 9, monomer conversion) and the

products, hexachlorethane, hexachloro-1, 3-butadiene and octachlorobutene-1, together with polymer oil, have been discussed in terms of an initial C - Cl bond split, with the chlorine atom acting as the carrier in a short chain process. In addition a ring closure scheme is mentioned to account for the formation of a chlorinated cyclohexadiene.

Allyl chloride was found to form a polymer, similar to that previously reported from studies with ultra-violet light, with an average degree of polymerisation equal to 5. Allyl bromide and allyl iodide gave negligible polymer formation. The results are discussed in terms of relative carbon-halogen bond strengths and mechanisms involving excited molecule formation and also homolytic bond split are mentioned briefly.

The products identified here, together with those previously reported from the radiolysis of benzene and toluene, are accommodated in a reaction scheme involving an initial C-H bond split followed by addition of hydrogen atoms and phenyl and benzyl radicals to the aromatic ring to form reactive intermediate cyclohexadienyl radicals. Alternative mechanisms are discussed.

A similar scheme was proposed to explain the results observed in the radiolysis of solutions of benzene and toluene in carbon tetrachloride. While chlorine atoms preferentially formed addition products with benzene (e.g. hexachlorocyclohexane), the analogous reaction involving toluene molecules yielded ring and side chain substitution products (e.g. chloro toluene and benzyl chloride). Only substitution reactions were observed involving the trichloromethyl radical (e.g. benzotrichloride from benzene, and benzyl chloroform and p-methyl benzotrichloride from toluene). Several reaction schemes are discussed in relation to yields of products, thermo-

chemical data, and the results reported by previous workers studying free radical attack on aromatic compounds. The major product from the radiation experiments was a mixture of high boiling unidentified products, the formation of which is discussed in terms of multiple radical attack on the intermediate cyclohexadienyl radical.

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